July 2004

Environmental Technology Verification Report

AANDERAA INSTRUMENTS, INC. RCM MK II WITH OPTODE 3830 MULTI-PARAMETER WATER QUALITY PROBE/SONDE

Prepared by
Battelle

Battelle
The Business of Innovation

In cooperation with the
National Oceanic and Atmospheric Administration

Under a cooperative agreement with

EPA U.S. Environmental Protection Agency

ETV ETV ETV

July 2004

Environmental Technology Verification Report

ETV Advanced Monitoring Systems Center

AANDERAA Instruments, Inc.
RCM Mk II with Optode 3830
Multi-Parameter Water Quality Probe/Sonde

by
Jeffrey Myers
Amy Dindal
Zachary Willenberg
Karen Riggs

Battelle
Columbus, Ohio 43201

and

Paul Pennington
Michael Fulton
Geoffrey Scott

NOAA CCEHBR
Charleston, South Carolina 29412

Notice

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Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's air, water, and land resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, the EPA's Office of Research and Development provides data and science support that can be used to solve environmental problems and to build the scientific knowledge base needed to manage our ecological resources wisely, to understand how pollutants affect our health, and to prevent or reduce environmental risks.

The Environmental Technology Verification (ETV) Program has been established by the EPA to verify the performance characteristics of innovative environmental technology across all media and to report this objective information to permitters, buyers, and users of the technology, thus substantially accelerating the entrance of new environmental technologies into the marketplace. Verification organizations oversee and report verification activities based on testing and quality assurance protocols developed with input from major stakeholders and customer groups associated with the technology area. ETV consists of seven environmental technology centers. Information about each of these centers can be found on the Internet at http://www.epa.gov/etv/.

Effective verifications of monitoring technologies are needed to assess environmental quality and to supply cost and performance data to select the most appropriate technology for that assessment. Under a cooperative agreement, Battelle has received EPA funding to plan, coordinate, and conduct such verification tests for "Advanced Monitoring Systems for Air, Water, and Soil" and report the results to the community at large. Information concerning this specific environmental technology area can be found on the Internet at http://www.epa.gov/etv/centers/center1.html.

Acknowledgments

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List of Abbreviations

AMS	Advanced Monitoring Systems
CCEHBR	Center for Coastal Environmental Health and Biomolecular Research
DAS	data acquisition system
DO	dissolved oxygen
DSU	data storage unit
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
L	liter
µM	microMolar
mg	milligram
mm	millimeter
NIST	National Institute of Standards and Technology
NOAA	National Oceanic and Atmospheric Administration
NTU	nephelometric turbidity unit
PE	performance evaluation
QA	quality assurance
QA/QC	quality assurance/quality control
QMP	Quality Management Plan
RSD	relative standard deviation
TSA	technical systems audit

Chapter 1
Background

The U.S. Environmental Protection Agency (EPA) has created the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized testing organizations; with stakeholder groups consisting of buyers, vendor organizations, and permitters; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance (QA) protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The EPA's National Exposure Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center recently evaluated the performance of the AANDERAA Instruments, Inc. RCM Mk II, housing the Optode 3830.

Chapter 2
Technology Description

The objective of the ETV AMS Center is to verify the performance characteristics of environmental monitoring technologies for air, water, and soil. This verification report provides results for the verification testing of the Mk II with Optode 3830 by AANDERAA Instruments, Inc. Following is a description of the Optode 3830, based on information provided by the vendor. The information provided below was not verified in this test.

Figure 2-1. AANDERAA Oxygen Optode 3830

The Optode 3830 (Figure 2-1) uses a platinum porphyrin complex as a dynamic fluorescence quencher to monitor oxygen in water. The porphyrin complex is embedded in a gas-permeable foil that is exposed to the surrounding water. A black optical isolation coating protects the complex from sunlight and fluorescent particles in the water. This sensing foil is attached to a sapphire window, providing optical access for the measuring system from inside a watertight titanium housing. The foil is excited by modulated blue light, and the phase of a returned red light is measured. By linearizing and temperature compensating with an incorporated temperature sensor, the absolute oxygen concentration can be determined. The diameter of the Optode 3830 is 36 millimeters (mm) (1.42 inches). It is 86 mm (3.39 inches) long and weighs 0.23 kilograms (8.11 ounces). Pricing information is available from the vendor.

The Mk II with Optode 3830 was verified for temperature, dissolved oxygen (DO), and turbidity. The range, resolution, and accuracy, as indicated by the vendor, for those parameters are listed below.

Table 2-1. Mk II with Optode 3830 Range, Resolution, and Accuracy as Provided by the Vendor

Parameter	Range	Resolution	Accuracy
Air saturation	0 to 120%	<0.4%	<5%
Oxygen concentration	0 to 500 µMolar (µM)	<1 µM	<8 µM or 5%, whichever is greater
Temperature	-2.7 to 36.6°C	0.1% of range	±0.05°C
Turbidity	0 to 20 nephelometric turbidity units (NTU)	0.1% of full scale	2% of full scale

Chapter 3
Test Design and Procedures

3.1 Introduction

This verification test was conducted according to procedures specified in the *Test/QA Plan for Long-Term Deployment of Multi-Parameter Water Quality Probes/Sondes*.(1) The purpose of the verification test was to evaluate the performance of the Mk II with Optode 3830 under realistic operating conditions. The Mk II with Optode 3830 was evaluated by determining calibration check accuracy and by comparing Mk II with Optode 3830 measurements with standard reference measurements and measurements from handheld calibrated probes. Two Mk II with Optode 3830s were deployed in saltwater, freshwater, and laboratory environments near Charleston, South Carolina, during a 3 ½-month verification test. Water quality parameters were measured both by the Mk II with Optode 3830 and by reference methods consisting of collocated field-portable instrumentation and analyses of collected water samples. During each phase, performance was assessed in terms of calibration check accuracy, relative bias, precision, linearity, and inter-unit reproducibility.

The performance of the Mk II with Optode 3830 was verified in terms of the following parameters:

- DO
- Temperature
- Turbidity.

3.2 Test Site Characteristics

The three test sites used for this verification were selected in an attempt to expose the Mk II with Optode 3830 to the widest possible range of conditions while conducting an efficient test. The three sites included one saltwater, one freshwater, and one controlled location. Approximate ranges for the target parameters at each of the test sites as determined by reference measurements are given in Table 3-1.

Table 3-1. Water Characteristics at the Test Sites

Parameter	Saltwater		Freshwater		Mesocosm	
	Low	High	Low	High	Low	High
DO	3milligrams/ liter (mg/L)	6 mg/L	6.8 mg/L	11.2 mg/L	9.3 mg/L	12.1 mg/L
Temperature	20°C	28°C	11°C	27°C	9°C	16°C
Turbidity	8 NTU	37 NTU	1.7 NTU	3.6 NTU	0.4 NTU	15 NTU

3.3 Test Design

The verification test was designed to assess the performance of multi-parameter water probes and was closely coordinated with the National Oceanic and Atmospheric Administration (NOAA) through the Center for Coastal Environmental Health and Biomolecular Research (CCEHBR). The test was conducted in three phases at a saltwater site in a tributary of Charleston Harbor; a freshwater site at the Hollings wetland on the CCEHBR campus; and a controlled site at the CCEHBR mesocosm facility in Charleston, South Carolina. At each test site, two Mk II with Optode 3830s were deployed as close to each other as possible to assess inter-unit reproducibility. The first phase of the test was conducted at the saltwater site (Figure 3-1). The CCEHBR campus has access to the tributary of Charleston Harbor site, which is a predominantly tidal body of water that receives some riverine input; its salinities range from 20 to 35 parts per thousand. The second phase of the test was conducted at the freshwater site (Figure 3-2). The freshwater site was a wetlands area near the Hollings Marine Research Laboratory, located on the CCHEBR campus. The third phase was conducted at the CCEHBR’s mesocosm facility (Figure 3-3). This facility contains modular mesocosms that can be classified as “tidal” or “estuarine.” The mesocosm phase included both saltwater and freshwater conditions.

The precision measurements were performed before the Mk II with Optode 3830 was deployed into the saltwater environment. The Mk II with Optode 3830 was placed in a tank of saline water inside the NOAA laboratory. While in this stable environment, the Mk II with Optode 3830 sampled at a rate of once per minute for approximately 30 minutes to collect data used in the percent relative standard deviation (RSD).

The schedule for the various testing activities is given in Table 3-2.

Figure 3-1. Saltwater Site

Figure 3-2. Freshwater Site

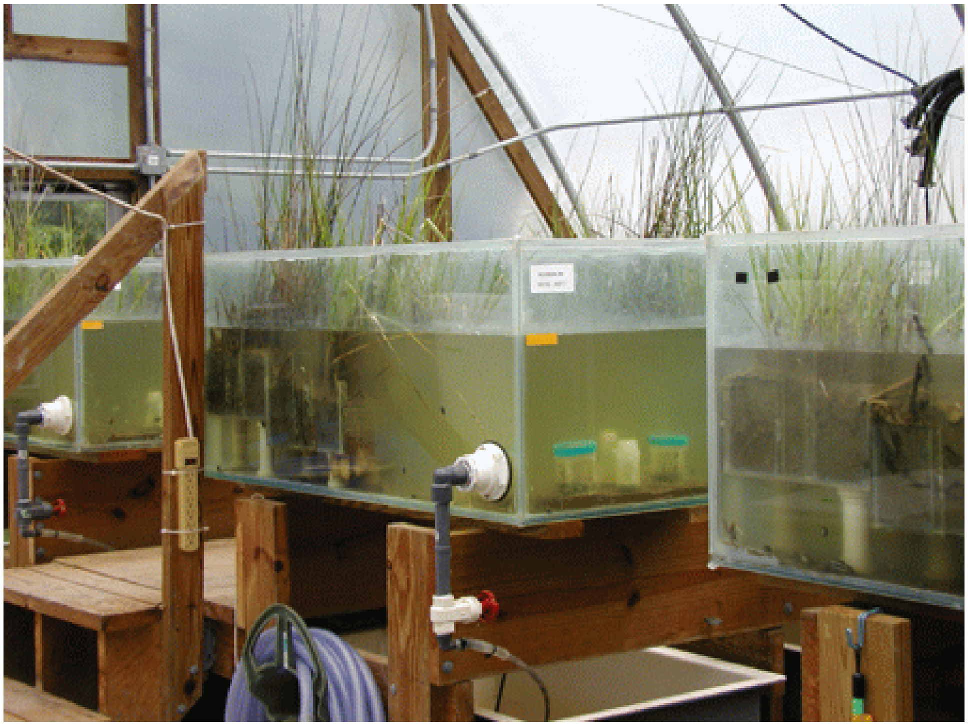


Figure 3-3. Mesocosm Tank

Table 3-2. Verification Test Schedule

Activity	Date
Vendor setup for saltwater phase	October 1, 2003
Begin saltwater phase	October 2, 2003
End saltwater phase	October 30, 2003
Set up freshwater phase	October 31, 2003
Begin freshwater phase	November 4, 2003
End freshwater phase	December 8, 2003
Vendor setup for mesocosm phase	December 9, 2003
Begin mesocosm phase	December 10, 2003
End mesocosm phase	January 5, 2004
Return all equipment	January 8, 2004

3.3.1 Saltwater Testing

The saltwater phase lasted for 28 days, during which time the Mk II with Optode 3830 monitored the naturally occurring range of the target parameters 24 hours per day at 10-minute measurement intervals. Dockside reference measurements were made for DO and temperature, while reference samples for turbidity were collected and returned to the laboratory for analysis. Figure 3-4 shows the Mk II with Optode 3830s at the pier. The Mk II with Optode 3830s were mounted on iron posts that were driven into the river bed. The Mk II with Optode 3830s were approximately 0.5 meters apart in the shallows of the tidal river. Reference samples were collected throughout the day during the test. For the duration of this phase, the Mk II with Optode 3830s were deployed at depths between approximately one and 10 feet, varying according to the tide. Table 3-3 shows the times and numbers of samples taken throughout the saltwater test phase.

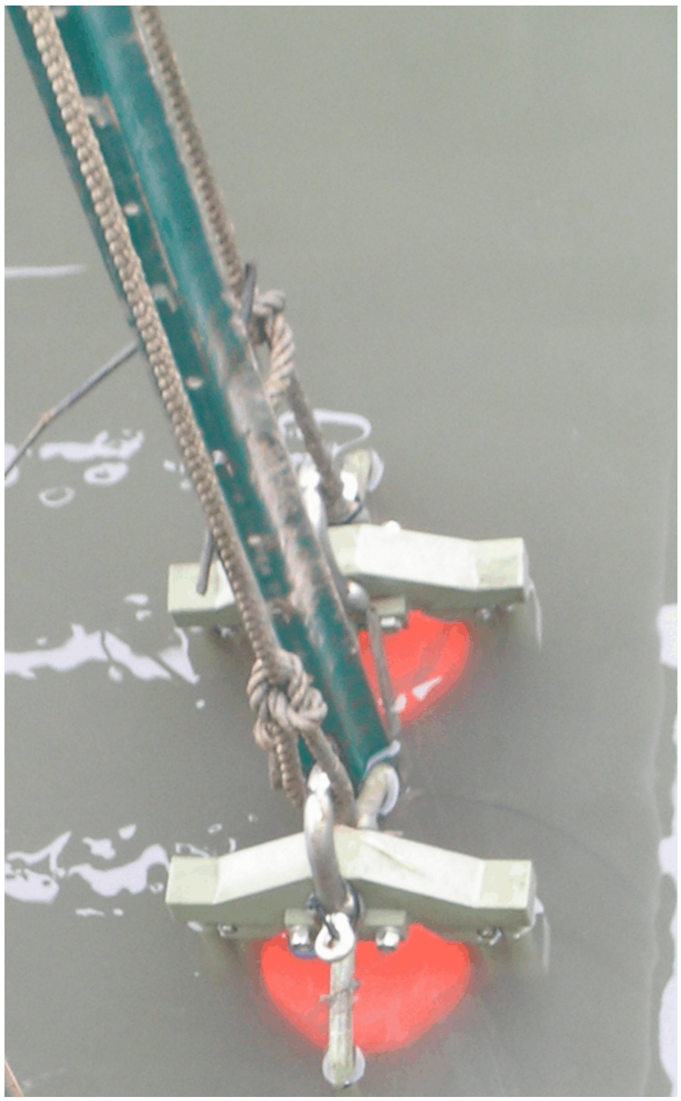


Figure 3-4. Saltwater Deployment

Table 3-3. Schedule for Saltwater Sample Collection—Tributary of Charleston Harbor

Test Day	Date	# Reference Samples	Activities
1	10/2/2003		Deploy Mk II with Optode 3830s
7	10/8/2003	2	
8	10/9/2003	4	
14	10/15/2003	4	
15	10/16/2003	4	
22	10/23/2003	6	
26	10/27/2003	9	
27	10/28/2003	6	
28	10/29/2003	6	
29	10/30/2003		Retrieve Mk II with Optode 3830s

3.3.2 Freshwater Testing

Freshwater testing was conducted at the wetlands on the CCEHBR campus and lasted 35 days. As in the saltwater portion of the verification test, the Mk II with Optode 3830 monitored the naturally occurring target parameters 24 hours per day, while reference measurements were made and turbidity reference samples collected, again rotating among collection times. Table 3-4 shows the sampling times and number of samples collected throughout the freshwater test phase. The Mk II with Optode 3830s were hung from a large post suspended several feet from the bottom of the pond.

During this portion of the deployment, the salinity and stratification of the freshwater pond increased. Natural weather and extreme tidal events caused the freshwater pond to become brackish and highly stratified. Reference measurements taken at varying depths along the water column during the first week of December showed significant stratification between the top and bottom of the freshwater pond. As a result, the freshwater phase at the Hollings wetlands was discontinued on December 8. The mesocosm deployment (Section 3.3.3) was extended to collect data using a freshwater deployment.

Table 3-4. Schedule for Freshwater Sample Collection—Hollings Wetlands

Test Day	Date	# Reference Samples	Activities
1	11/4/2003		Deploy Mk II with Optode 3830s
2	11/5/2003	6	
3	11/6/2003	9	
4	11/7/2003	6	
17	11/20/2003	9	
30	12/03/2003	9	
36	12/08/2003	16	Retrieve Mk II with Optode 3830s

3.3.3 *Mesocosm Testing*

Mesocosm testing was performed over 27 days according to the schedule shown in Table 3-5. Reference measurements were made and water samples were collected during each test day throughout the normal operating hours of the facility (nominally 6 a.m. to 6 p.m.). During this phase, the mesocosm was manipulated to introduce variations in the measured parameters. The turbidity of the system was varied by operating a pump near the sediment trays to suspend additional solids in the water. During the last three weeks of testing, saltwater was drained and replaced with freshwater. These activities are detailed in Table 3-5.

Table 3-5. Schedule for Mesocosm Sample Collection

Test Day	Date	# Reference Samples	Activities
1	12/10/2003	4	Deploy Mk II with Optode 3830s in saltwater
3	12/12/2003	6	10:00 - Transition to freshwater (to change conductivity)
4	12/13/2003		Begin freshwater portion of deployment
6	12/15/2003	4	11:05 - Turn off air bubblers and turn off circulation pump
7	12/16/2003	4	10:40 - Turn on circulation pump 10:50 - Add mud slurry (to change turbidity) 13:00 - Add additional mud slurry 15:11 - Turn off circulation pump
8	12/17/2003	5	
9	12/18/2003	2	
24	1/2/2004	3	10:20 - Turn on air bubblers (to change DO)
27	1/5/2004	3	Retrieve Mk II with Optode 3830s

Variations in temperature and DO were driven by natural forces. Parameters over the ranges specified in Table 3-1 were monitored by the Mk II with Optode 3830. Samples were collected and analyzed using a reference method for comparison.

3.4 Reference Measurements

The reference measurements made in this verification test and the equipment used for these measurements were as follows:

- DO—National Institute of Standards and Technology (NIST)-traceable, commercially available probe (Orion 830A)
- Temperature—NIST-traceable, handheld thermocouple and readout (Orion 830A)
- Turbidity—Hach Ratio XR turbidity meter (Hach 43900).

Reagents were distilled deionized water (for field blanks) and a Hach Ratio XR turbidity standard from Advanced Polymer Systems. Sampling equipment consisted of 0.5- to 1.0-L glass bottles, a Niskin sampling device provided by CCEHBR, and provisions for sample storage. The maximum sample holding times are given in Table 3-6. All sample holding time requirements were met.

Table 3-6. Maximum Sample Holding Times

Parameter	Holding Time
DO	none[a]
Temperature	none
Turbidity	24 hours

[a] "None" indicates that the sample analyses must be performed immediately after sample collection or in the water column at the site.

Chapter 4
Quality Assurance/Quality Control

Quality assurance/quality control (QA/QC) procedures were performed in accordance with the quality management plan (QMP) for the AMS Center[2] and the test/QA plan for this verification test.[1]

4.1 Instrument Calibration

Both the portable and laboratory reference instruments were calibrated by CCEHBR according to the procedures and schedules in place at the test facility, and documentation was provided to Battelle.

4.2 Field Quality Control

Replicate samples were taken during field sampling for assessment of the reference methods. The replicate samples were collected once each week during a regular sampling period by splitting field samples into two separate samples (containers) and analyzing both by the same laboratory reference methods. The results from the replicate analysis and the field blanks met the criteria listed in Tables 4-1 and 4-2, respectively. A container of deionized water (field blank) was taken to the field, brought back to the laboratory, and analyzed in the same manner as the collected samples.

4.3 Sample Custody

Samples collected at the saltwater, freshwater, and mesocosm sites were transported by the scientist performing the sampling at CCEHBR to the laboratory in an ice-filled cooler and analyzed immediately; therefore, no chain-of-custody forms were required.

Table 4-1. Replicate Analysis QC Criteria

Parameter	Observed Agreement
DO	±5%
Temperature	±1°C
Turbidity	±5 NTU

Table 4-2. Expected Values for Field Blanks

Parameter	Observed Maximum Difference
Turbidity	1 NTU

4.4 Audits

4.4.1 Performance Evaluation Audit

A performance evaluation (PE) audit was conducted by the Battelle Test Coordinator once during the verification test to assess the quality of the reference measurements. For the PE audit, independent standards were used. Table 4-3 shows the procedures used for the PE audit and associated results.

Table 4-3. Summary of Performance Evaluation Audits

Audited Parameter	Audit Procedure	Acceptable Tolerance	Actual Difference	Passed Audit
DO	Oakton 100 monitor	±5%	1.1%	Yes
Temperature	Orion 230 thermometer	±1°C	0.0 °C	Yes
Turbidity	Advanced Polymer Systems turbidity standard	±10%	0.72%	Yes

The DO measurement made by the Orion 830A was compared with that from a handheld DO Oakton 100 monitor. Agreement within 1.1% was achieved. The comparison was made with a sample of collected water, and agreement was within 0.0°C. A NIST-traceable Orion 230 thermometer was used for the temperature performance audit. The Hach turbidity meter measurements were compared with an independent turbidity standard. Agreement within 0.72% was observed.

4.4.2 Technical Systems Audit

The Battelle Quality Manager conducted a technical systems audit (TSA) on October 28, 2003, to ensure that the verification test was performed in accordance with the test/QA plan(1) and the AMS Center QMP.(2) As part of the audit, the Battelle Quality Manager reviewed the reference methods used, compared actual test procedures to those specified in the test/QA plan, and reviewed data acquisition and handling procedures. Observations and findings from this audit were documented and submitted to the Battelle Verification Test Coordinator for response. The records concerning the TSA are permanently stored with the Battelle Quality Manager.

During the verification test, two deviations from the test/QA plan were necessary. The first occurred when natural weather events caused the freshwater pond to become brackish and highly stratified, resulting in reference measurements that were not representative of the water the Mk II with 3830 measured. An extended freshwater period, beginning on December 13, 2003, was added to the end of mesocosm deployment to provide data from a freshwater deployment. Therefore, relative bias and linearity data were not collected at the freshwater site. The data were collected from the mesocosm extension instead. The second deviation occurred when a problem with the Niskin sampler developed. The sampler broke after several uses at the beginning of the saltwater period and was replaced as soon as possible. However, this malfunction resulted in fewer reference samples. The deviations had no impact on the results of the test.

4.4.3 Audit of Data Quality

At least 10% of the data acquired during the verification test was audited. Battelle's Quality Manager traced the data from the initial acquisition, through reduction and statistical analysis, to final reporting, to ensure the integrity of the reported results. All calculations performed on the data undergoing the audit were checked.

4.5 QA/QC Reporting

Each assessment and audit was documented in accordance with Sections 3.3.4 and 3.3.5 of the QMP for the ETV AMS Center.[2] Once the assessment report was prepared, the Verification Test Coordinator ensured that a response was provided for each adverse finding or potential problem and implemented any necessary follow-up corrective action. The Battelle Quality Manager ensured that follow-up corrective action was taken. The results of the TSA were sent to the EPA.

4.6 Data Review

Records generated in the verification test were reviewed within two weeks of generation before these records were used to calculate, evaluate, or report verification results. Table 4-4 summarizes the types of data recorded. The review was performed by a Battelle technical staff member involved in the verification test, but not the staff member who originally generated the record. The person performing the review added his/her initials and the date to a hard copy of the record being reviewed.

Table 4-4. Summary of Data Recording Process

Data to be Recorded	Responsible Party	Where Recorded	How Often Recorded	Disposition of Data[(a)]
Dates, times of test events	CCEHBR	Laboratory record books/data sheets	Start/end of test; at each change of a test parameter; at sample collection	Used to organize/check test results; manually incorporated data into spreadsheets - stored in test binder
Test parameters	Battelle/ CCEHBR	Laboratory record books/data sheets	Each sample collection	Used to organize/check test results; manually incorporated data into spreadsheets - stored in test binder
Mk II with Optode 3830 data - digital display - electronic output	 CCEHBR CCEHBR	 Data sheets Probe data acquisition system (DAS); data stored on probe down-loaded to personal computer	 Continuous 10-minute sampling; data downloaded to personal computer	Used to organize/check test results; incorporated data into electronic spreadsheets - stored in test binder
Reference monitor readings/reference analytical results	CCEHBR	Laboratory record book/data sheets or data management system, as appropriate	After each batch sample collection; data recorded after reference method performed	Used to organize/check test results; manually incorporated data into spreadsheets - stored in test binder
Reference calibration data	CCEHBR	Laboratory record books/data sheets/DAS	Whenever zero and calibration checks are done	Documented correct performance of reference methods - stored in test binder
PE audit results	Battelle	Laboratory record books/data sheets/DAS	At times of PE audits	Test reference methods with independent standards/measurements - stored in test binder

(a) All activities subsequent to data recording were carried out by Battelle.

Chapter 5
Statistical Methods

The statistical methods presented in this chapter were used to verify the performance parameters listed in Section 3.1.

5.1 Calibration Check Accuracy

The Mk II with Optode 3830 was calibrated for each measured parameter at the beginning and end of each deployment period according to the vendor's instruction manual. The results from the calibration checks were summarized, and accuracy was determined each time the calibration check was conducted. Calibration check accuracy (*A*) is reported as a percentage, calculated using the following equation:

$$A=1-(C_s-C_p)/C_s \text{ x } 100 \qquad (1)$$

where C_s is the value of the reference standard, and C_p is the value measured by the Mk II with Optode 3830. The closer *A* is to 100, the more consistent the calibration check accuracy.

5.2 Relative Bias

Water samples were analyzed by both the reference method and the Mk II with Optode 3830, and the results were compared. The results for each sample were recorded, and the accuracy was expressed in terms of the average relative bias (*B*), as calculated from the following equation:

$$B = \frac{C_R - C_P}{C_R} \text{ x } 100 \qquad (2)$$

where C_P is a measurement taken from the Mk II with Optode 3830 being verified at the same time as the reference measurement was taken, and C_R is the reference measurement. This calculation was performed for each reference sample analysis for each of the three target water parameters. In addition, relative bias was assessed independently for each Mk II with Optode 3830 to determine inter-unit reproducibility.

5.3 Precision

The standard deviation (*S*) of the measurements made during a period of stable operation at the mesocosm was calculated and used as a measure of probe precision:

$$S = \left[\frac{1}{n-1} \sum_{k=1}^{n} (C_k - \overline{C})^2 \right]^{1/2} \tag{3}$$

where n is the number of replicate measurements, C_k is the concentration reported for the k^th measurement, and $\overline{C}$ is the average concentration of the replicate measurements.

Precision was calculated for each of the three target water parameters. Probe precision was reported in terms of the percent RSD of the series of measurements.

$$\%\text{RSD} = \frac{S}{\overline{C}} \text{ x } 100 \tag{4}$$

5.4 Linearity

For target water parameters, linearity was assessed by linear regression, with the analyte concentration measured by the reference method as an independent variable and the reading from the analyzer verified as a dependent variable. Linearity is expressed in terms of the slope, intercept, and coefficient of determination (R^2). Linearity was assessed separately for each Mk II with Optode 3830.

5.5 Inter-Unit Reproducibility

The results obtained from the two Mk II with Optode 3830s were compiled independently and compared to assess inter-unit reproducibility. Inter-unit reproducibility was determined by calculating the average absolute difference between the two Mk II with Optode 3830s. In addition, the two Mk II with Optode 3830s were compared by evaluating the relative bias of each.

Chapter 6
Test Results

The results of the verification of the two Mk II with Optode 3830s (identified as 1103 and 1104 in this report) are presented in this section. The Mk II with Optode 3830 data were recorded at 10-minute intervals throughout the verification test. First, a visual record of the condition of the Mk II with Optode 3830s pre- and post-deployment is discussed, then the statistical comparisons are made. Finally, a record of the activities involved in servicing and maintenance of the Mk II with Optode 3830s is presented.

Prior to the initial saltwater deployment, the Mk II with Optode 3830s were in “like-new” condition. That is, they arrived from the vendor crated and ready for installation. Figure 6-1 shows one of the two Mk II with Optode 3830s in its pre-deployment condition. As deployed, the end where the individual probes are placed is exposed and oriented on top of the probe.

Figure 6-1. Mk II with Optode 3830 Prior to Deployment. Starting at the top center and proceeding clockwise: (1) close-up of clean Mk II with housing removed, (2) close-up of Optode 3830, (3) clean turbidity probe, (4) data storage unit, (5) Mk II dock with housing and protective side bars.

Following the saltwater deployment, the Mk II with Optode 3830s were retrieved from the water and immediately returned to the laboratory to record the post-deployment condition. Figure 6-2 shows the post-deployment condition of the Mk II with Optode 3830s. The Mk II with Optode 3830s were covered with a combination of green algae, silt, and some shell growth.

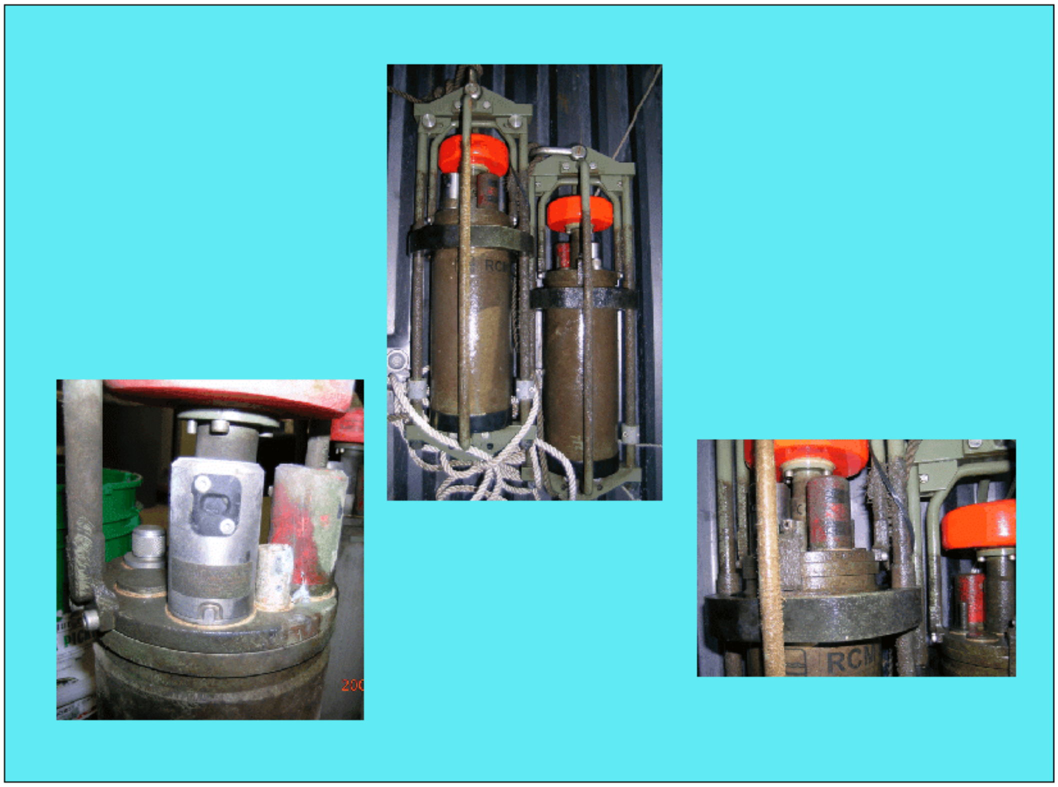


Figure 6-2. Mk II with Optode 3830 After Saltwater Deployment. Both Mk II with Optode 3830s after being removed from the saltwater deployment (top), with close-ups of Mk II with Optode 3830 (left) and turbidity probe (right).

Prior to redeployment at the freshwater location, the Mk II with Optode 3830s were cleaned. This consisted of gently rubbing the optical windows of the turbidity and oxygen probes with a towel and 10% acetic acid solution. Then the Mk II with Optode 3830s were placed overnight in a tank of oxygen-saturated water before deployment. Figure 6-3 shows the cleaned and reconditioned Mk II with Optode 3830s in this tank.

Figure 6-3. Cleaned and Reconditioned Mk II with Optode 3830 in Storage Tank Used Between Deployments

Finally, the condition of the Mk II with Optode 3830s after the freshwater deployment was recorded and is shown in Figure 6-4. As can be seen from the photos, the Mk II with Optode 3830s appeared more fouled after the saltwater deployment than after the freshwater deployment, both from biofouling and small marine life.

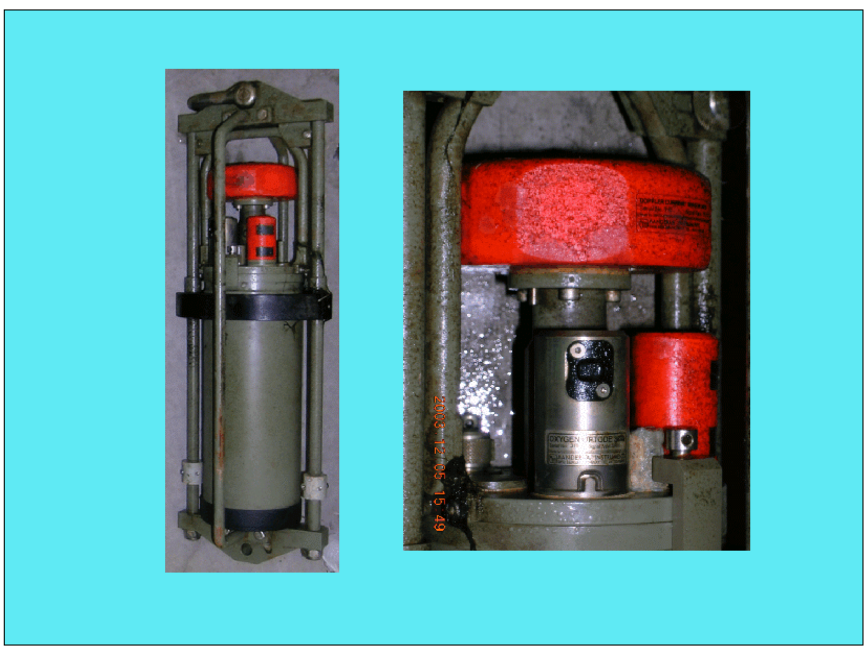


Figure 6-4. Mk II with Optode 3830 After Freshwater Deployment, with Close-up of Mk II with Optode 3830 (right)

6.1 Calibration Check Accuracy

The Mk II with Optode 3830s were calibrated only at the beginning of the test. The calibrations were checked at the end of each deployment as instructed by the vendor. No check was performed for temperature. Table 6-1 shows the results from these calibration checks for the saltwater, freshwater, and mesocosm tests.

Table 6-1. Calibration Check Accuracy

Deployment Location	Date	Calibration Check Accuracy (%)			
		1103		1104	
		DO	Turbidity	DO	Turbidity
Saltwater	10/29/2003	98.9	30	97.3	18
Freshwater	12/9/2003	98.9	1,500	95.6	800
Mesocosm	1/13/2004	99.7	NA[a]	83.9	520

[a] Saturated; no data reported.

The accuracy shown in Table 6-1 is the comparison of how well the Mk II with Optode 3830s held their calibration throughout the verification test. The Mk II with Optode 3830s were factory calibrated; and, therefore, no adjustments to the calibrations were made during the verification test. As shown in the table, the turbidity calibration check did not correlate well with the initial calibration values. The Mk II with Optode 3830, as tested, used a turbidity probe that had a maximum range of 20 NTU, which is designed for the most common use of these probes—open ocean waters.

The calibration check accuracy for DO was consistently greater than 98.9% for the 1103. The 1104 measurements were consistently lower than the 1103 from the first day of deployment and had a calibration check accuracy ranging from 83.9 to 97.3%.

6.2 Relative Bias

Relative bias (the percent difference between the Mk II with Optode 3830 measurements and the reference measurements) was assessed by comparing the reference measurements with the 1103 and 1104 readings. The Mk II with Optode 3830 reading that was closest in time to the reference sample was used. Plots of the 1103 and 1104 data, along with the corresponding reference measurements that were used for the relative bias calculations, are shown in Figures 6-5a-f.

No data are reported for the freshwater period because of the stratification that occurred. The relative bias results are summarized in Table 6-2. The temperature measurements resulted in a relative bias that was below 2% throughout the test. The oxygen relative accuracy was below 20% throughout the saltwater deployment and below 10% throughout the mesocosm deployment. During saltwater deployment, the turbidity probe exhibited higher bias because the deployment conditions sometimes exceeded the Mk II with Optode 3830 range. These results

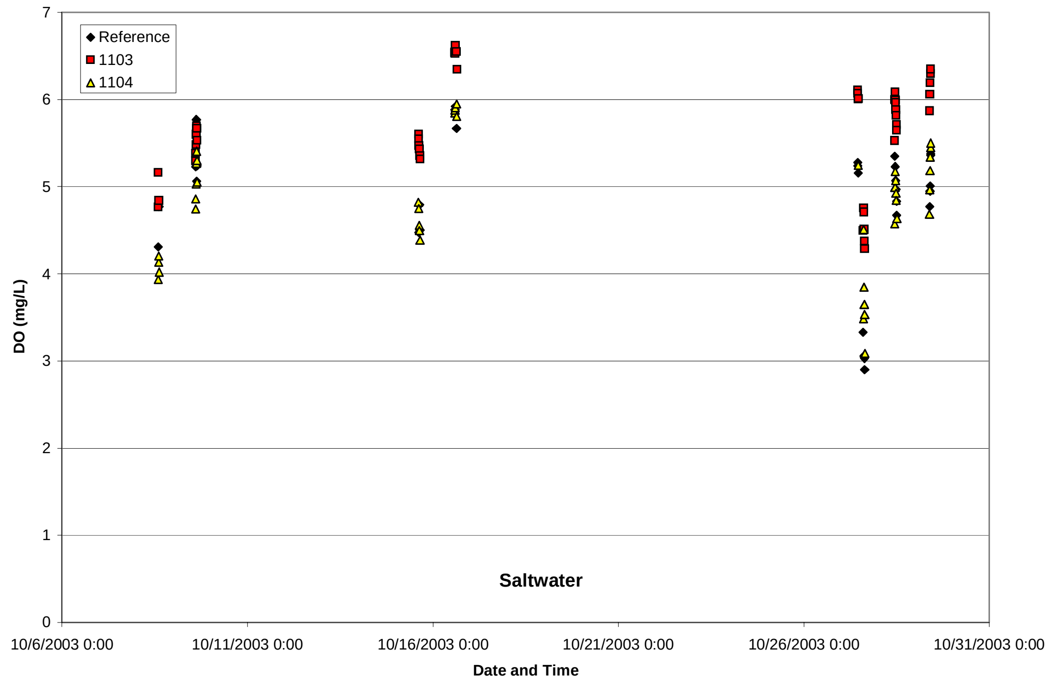


Figure 6-5a. Relative Bias Data for DO (Saltwater)

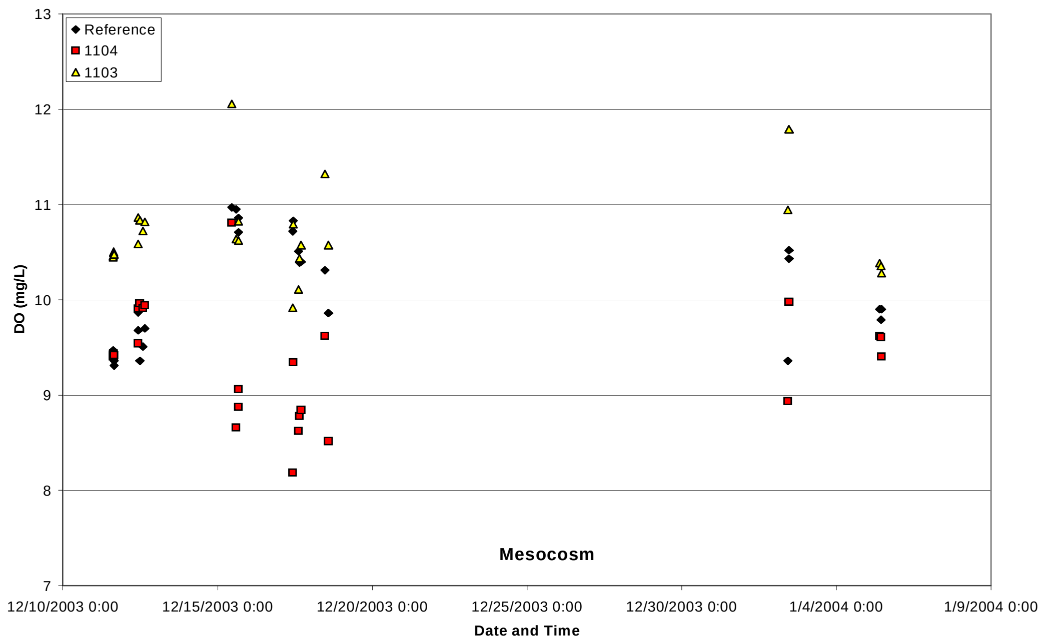


Figure 6-5b. Relative Bias Data for DO (Mesocosm)

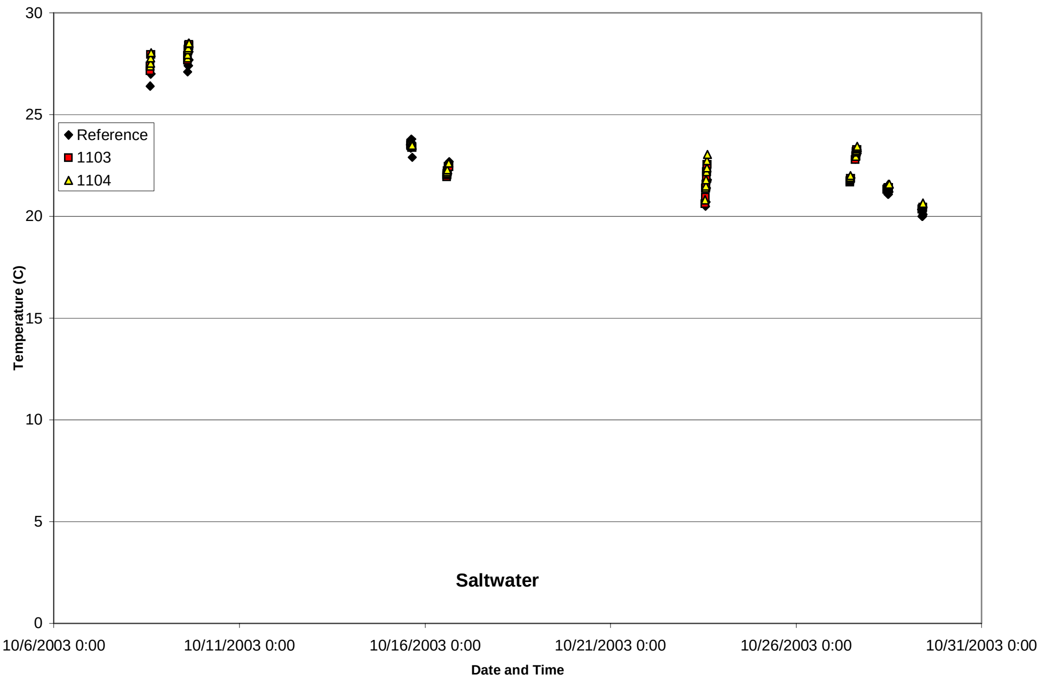


Figure 6-5c. Relative Bias Data for Temperature (Saltwater)

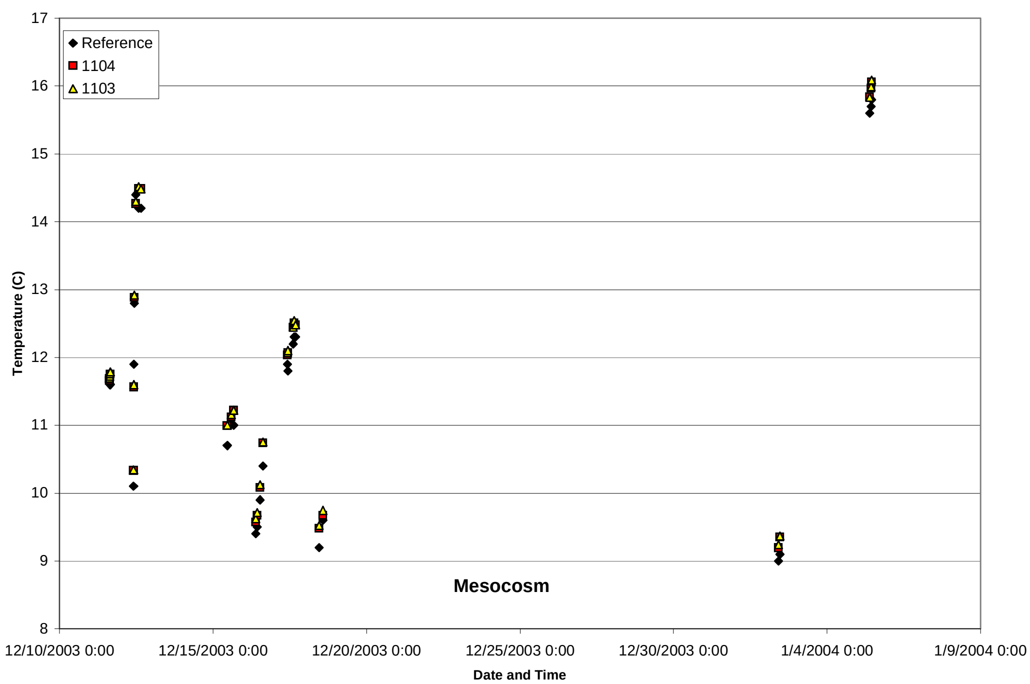


Figure 6-5d. Relative Bias Data for Temperature (Mesocosm)

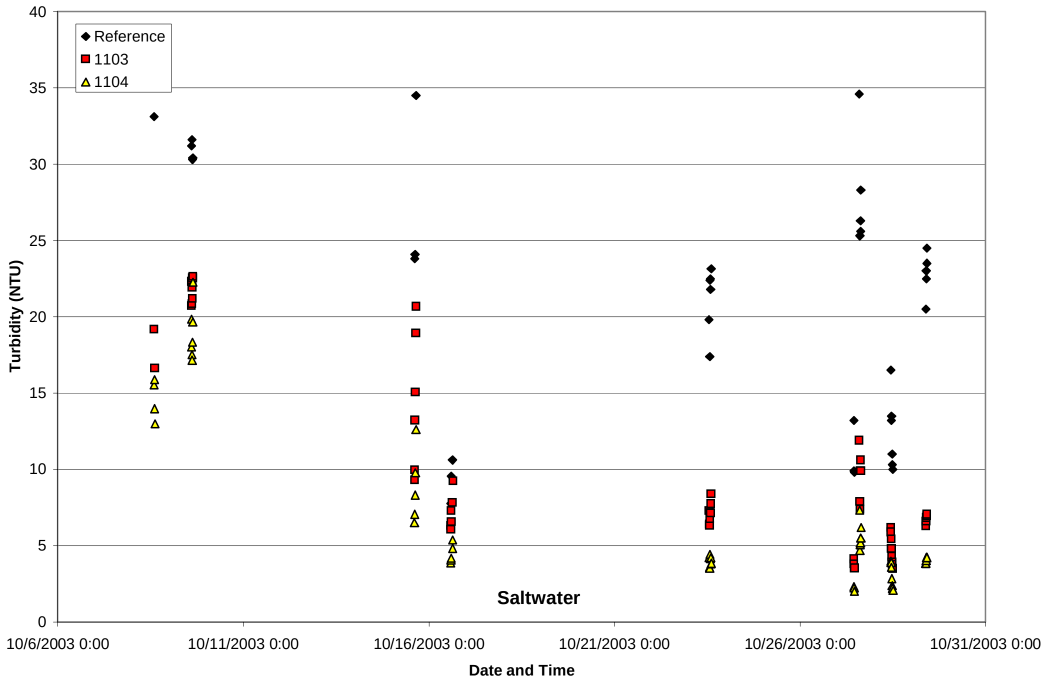


Figure 6-5e. Relative Bias Data for Turbidity (Saltwater)

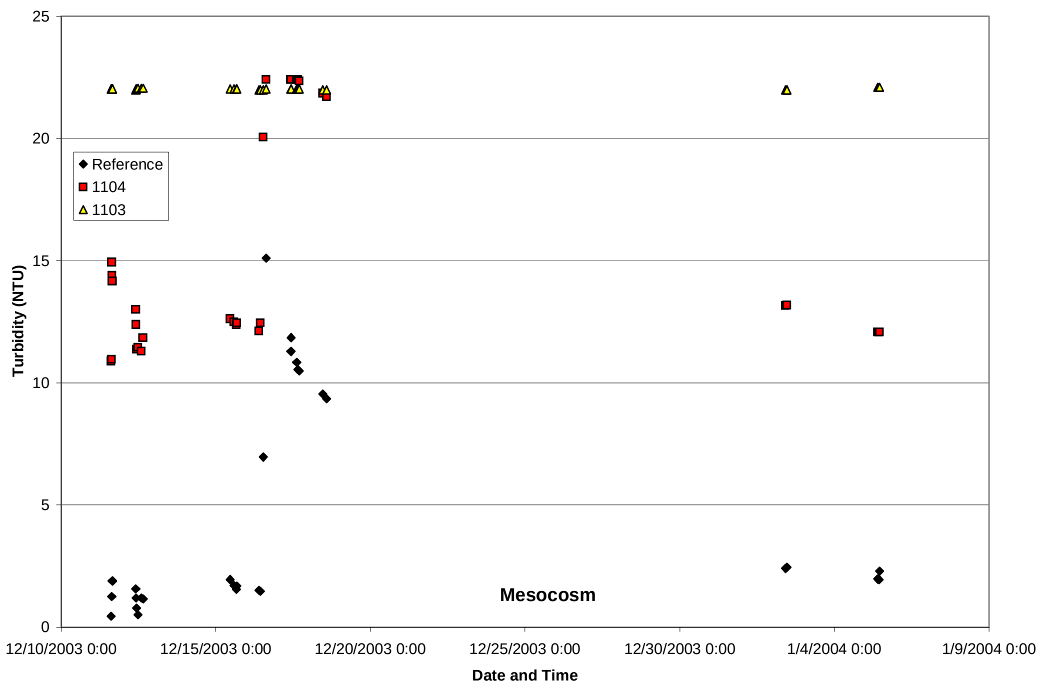


Figure 6-5f. Relative Bias Data for Turbidity (Mesocosm)

Table 6-2. Average Relative Bias Results for 1103 and 1104

	Saltwater		Mesocosm	
Parameter	**1103 (%)**	**1104 (%)**	**1103 (%)**	**1104 (%)**
DO	-19.7	-13.8	-6.79	6.61
Temperature	-0.99	-1.76	-1.76	-1.51
Turbidity	54.2	69.0	-521	-452

occurred during deployments where the parameter being measured changed throughout the day. Since the MkII with Optode 3830 recorded at intervals of 10 minutes, there could have been as much as 5 minutes' difference between the time of the reference sample and the nearest recorded Mk II with Optode 3830 data. Because of this temporal effect, between 1% and 3% of the relative bias calculations may be attributable to the differences seen between the two measurements. In addition, when combined with the manufacturer's specifications for the accuracy of the reference measurements of 2%, a total of up to 5% difference may be due to the combined temporal effects and inherent accuracy of the reference measurements.

6.3 Precision

Table 6-3 shows the results of calculations taken from measurements performed before the saltwater deployment. The precision, reported as %RSD, was less than 3% for temperature and DO. Data from turbidity resulted in higher %RSDs (24.4 and 26.8) possibly as a result of the fact that measurements were near the zero point and particles moving into the detector's view would cause a measurement to spike, despite all attempts to keep the test conditions constant.

Table 6-3. Measurements and Percent Relative Standard Deviations for 1103 and 1104 During Stable Mesocosm Operation

	1103			1104		
	DO (mg/L)	**Temperature (°C)**	**Turbidity (NTU)**	**DO (mg/L)**	**Temperature (°C)**	**Turbidity (NTU)**
Maximum	308	17.8	2.3	314	17.7	2.5
Minimum	294	16.4	0.387	305	16.2	0.387
Standard Deviation	3.99	0.377	0.38	2.32	0.474	0.35
Average	303	17.1	1.41	311	16.9	1.45
%RSD	1.32	2.20	26.8	0.73	2.80	24.4

6.4 Linearity

Linearity was assessed by comparing probe readings against the reference values for each of the parameters at each deployment location. Figures 6-6a-f give the results of this comparison by showing the slope, intercept, and coefficient of determination (R^2) for each parameter. Linearity and regression coefficients indicated the best agreement between the Mk II with Optode 3830 readings and reference values for temperature. During the saltwater deployment, the DO measurements resulted in slopes between 0.70 and 0.74 and regression coefficients between 0.76 and 0.79 over a range of 3 to 6 mg/L. During the mesocosm deployment, the Mk II with Optode 3830 demonstrated less linear behavior, with the slopes and regression coefficients both decreasing for DO. Finally, when the turbidity sensor was within its working range and not obstructed (as was 1103 during the mesocosm deployment), the measurements resulted in a slope of 0.99 and a regression coefficient of 0.93 over a range of 0.4 to 15 NTU.

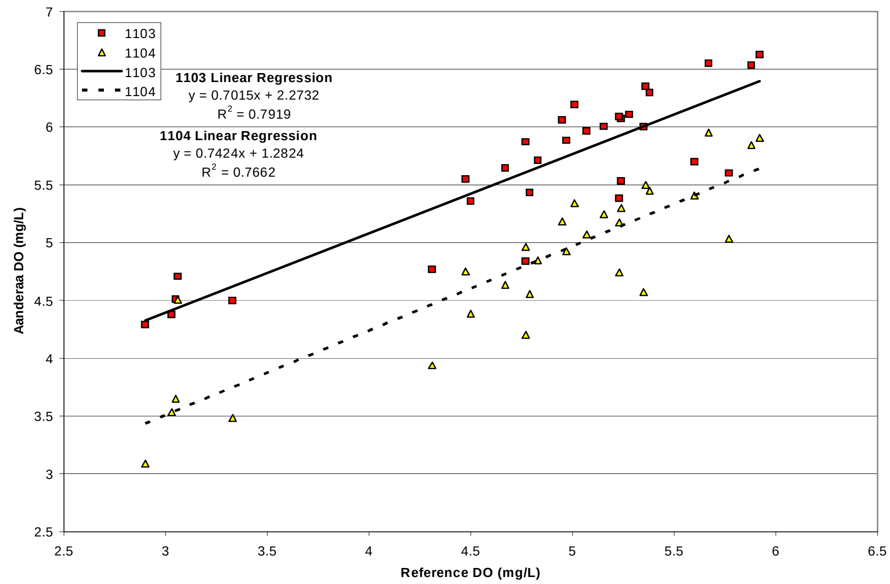


Figure 6-6a. Linearity Data for DO (Saltwater)

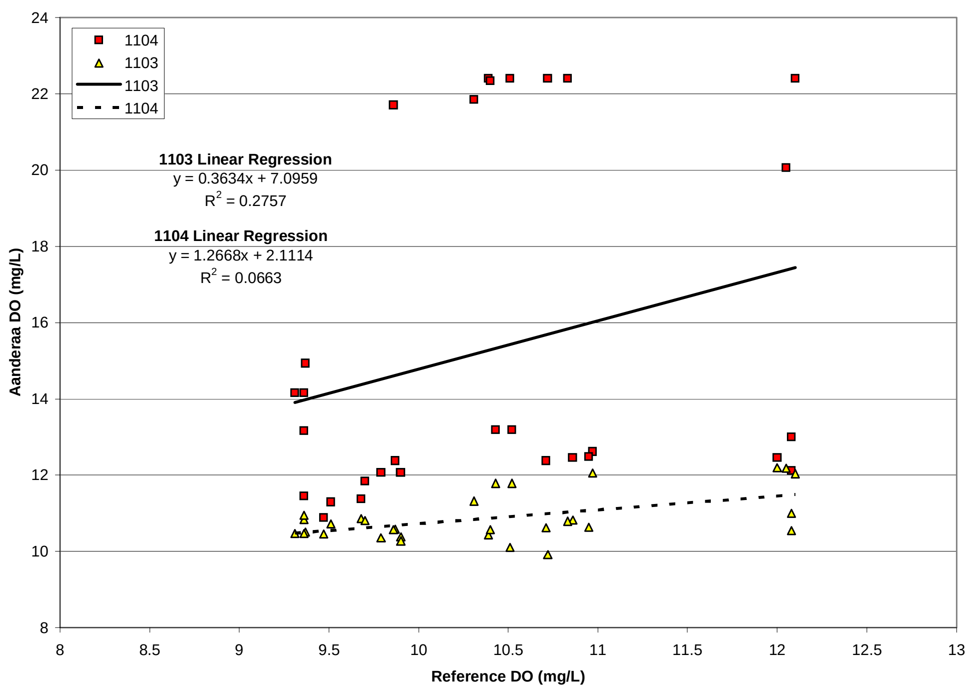


Figure 6-6b. Linearity Data for DO (Mesocosm)

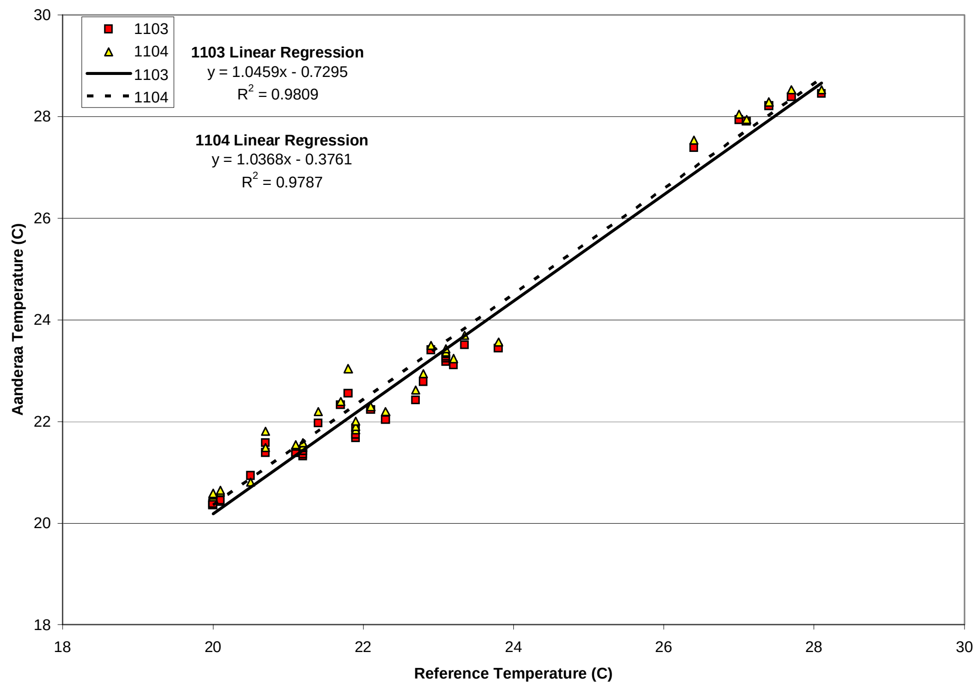


Figure 6-6c. Linearity Data for Temperature (Saltwater)

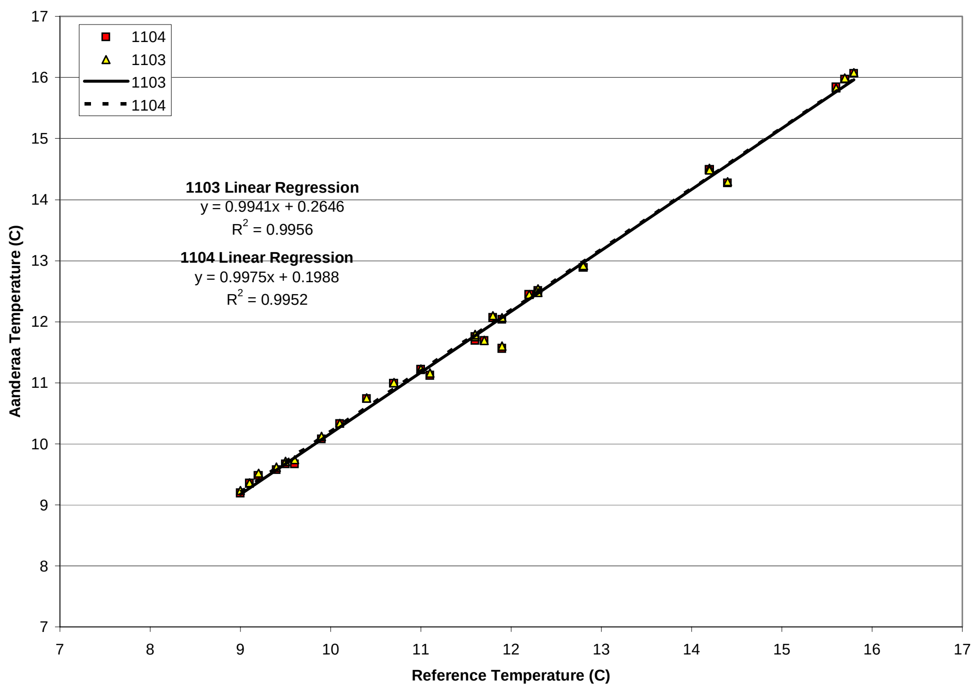


Figure 6-6d. Linearity Data for Temperature (Mesocosm)

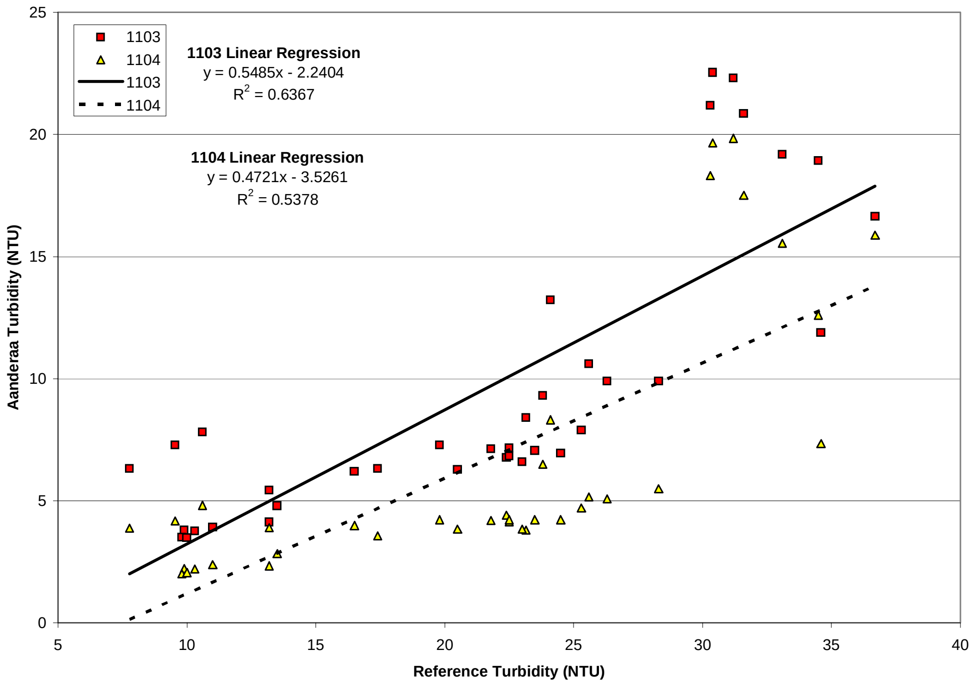


Figure 6-6e. Linearity Data for Turbidity (Saltwater)

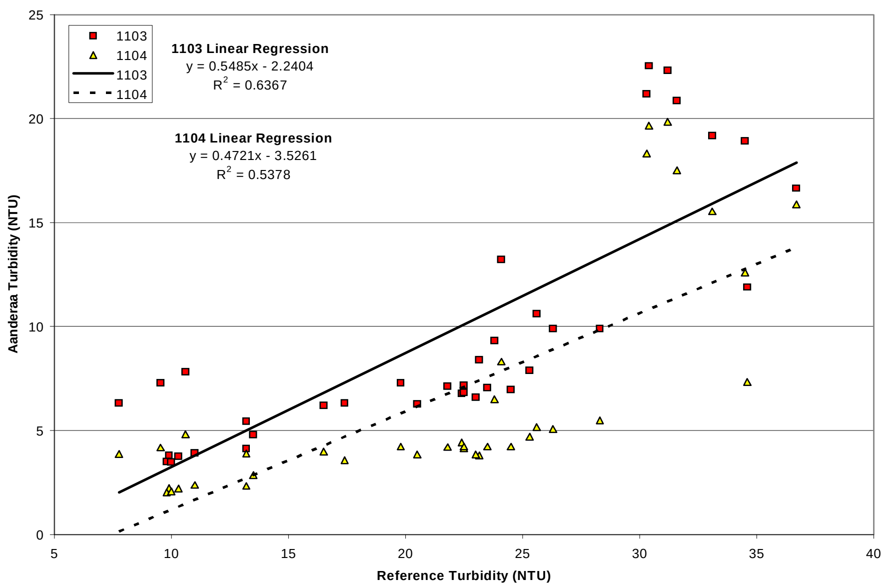


Figure 6-6f. Linearity Data for Turbidity (Mesocosm)

6.5 Inter-Unit Reproducibility

Inter-unit reproducibility was assessed both by comparing the relative bias of the two Mk II with Optode 3830s (Section 6.2) and by comparing the average absolute differences between the two Mk II with Optode 3830 readings for each parameter at each deployment location. Freshwater results are included because the two Mk II with Optode 3830s were deployed to the same depth. Figures 6-7 through 6-9 show the data used for these calculations. These calculations were made for the readings where there was an analogous reference measurement only. The results of average difference comparisons are shown in Table 6-4, where "n" is the number of measurements.

Table 6-4. Average Absolute Difference Between 1103 and 1104 Readings for Each Parameter at Each Deployment Location

	Average Absolute Difference Between 1103 and 1104 Readings					
Location	DO (mg/L)	n	Temperature (°C)	n	Turbidity (NTU)	n
Saltwater	1.02	3,328	0.16	4,192	3.12	4,192
Freshwater	1.42	5,188	0.04	5,188	10.9	5,188
Mesocosm	1.78	3,888	0.03	3,888	7.26	3,888
Average	1.41		0.08		7.08	

The DO difference between the two Mk II with Optode 3830s tested averaged 1.41 mg/L (Figures 6-7a-c). The average difference in temperature readings was 0.08°C. The average difference in turbidity readings was 7.08 NTU.

The magnitude of the inter-unit reproducibility results for turbidity was affected by the apparent saturation of the 1103 sensor during the freshwater test.

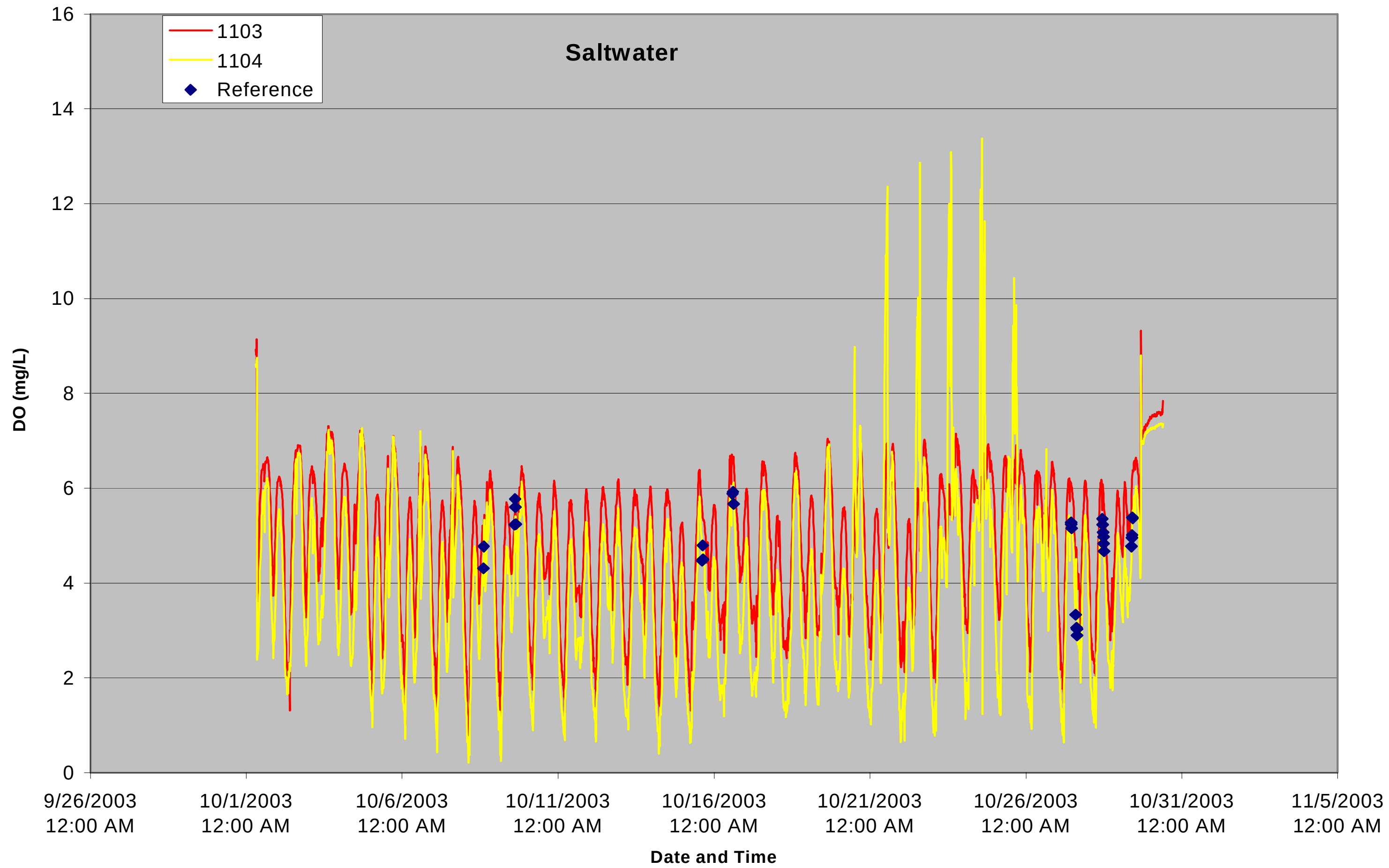


Figure 6-7a. Inter-Unit Reproducibility Data for DO During Saltwater Tests (Between October 20 and October 26, 2003, extremely low tides caused the equipment to come out of the water.)

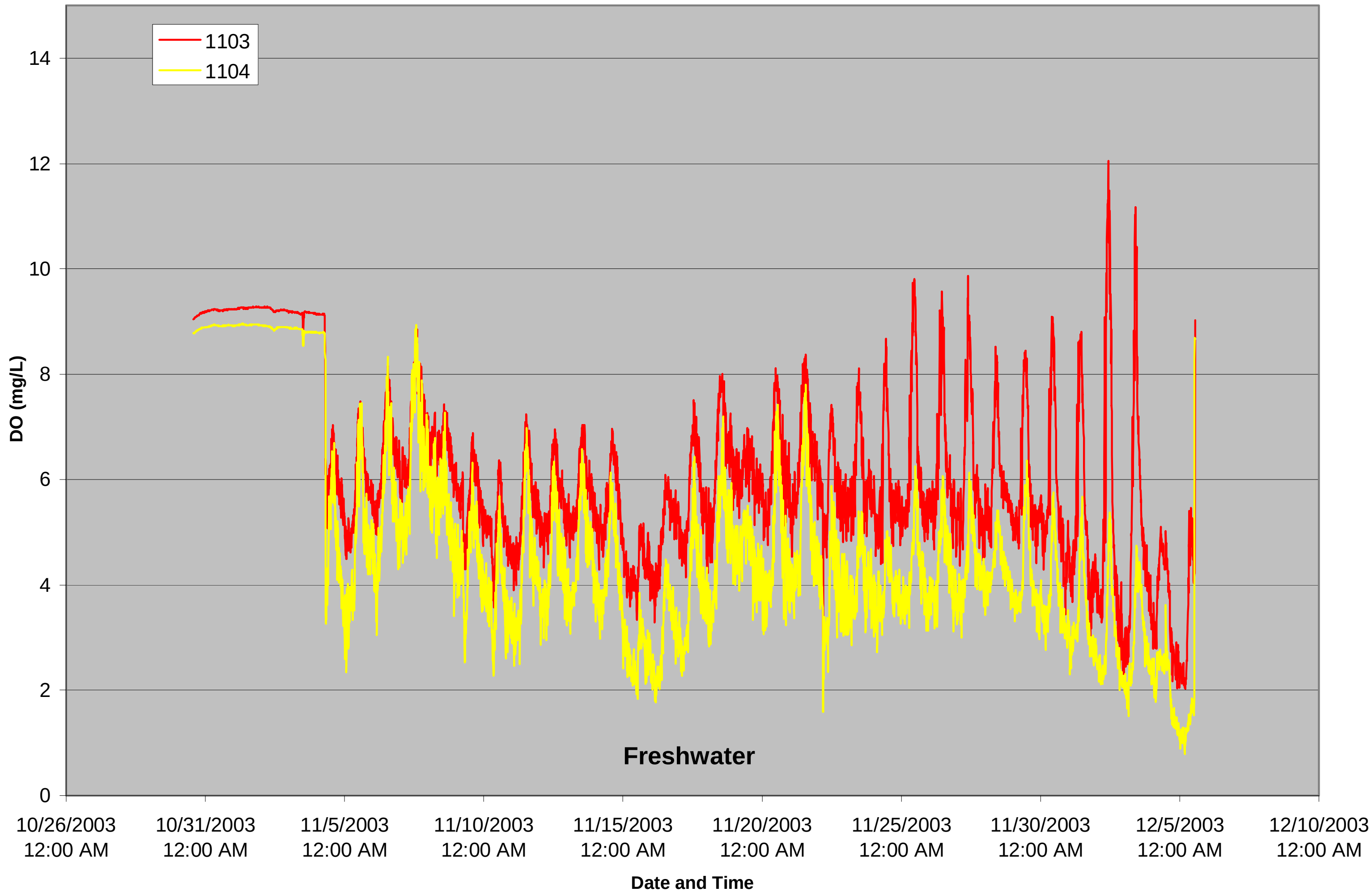


Figure 6-7b. Inter-Unit Reproducibility Data for DO During Freshwater Tests

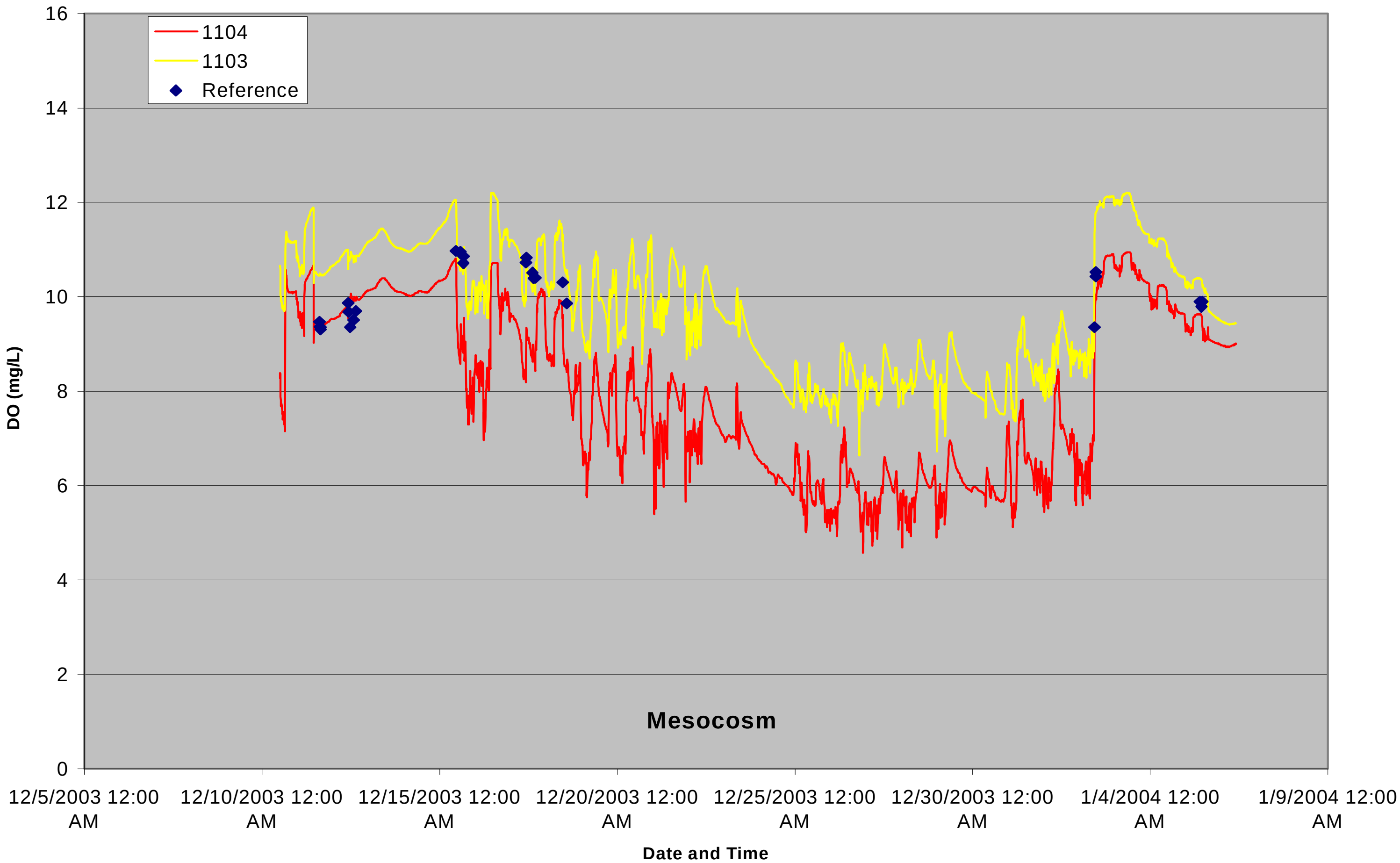


Figure 6-7c. Inter-Unit Reproducibility Data for DO During Mesocosm Tests

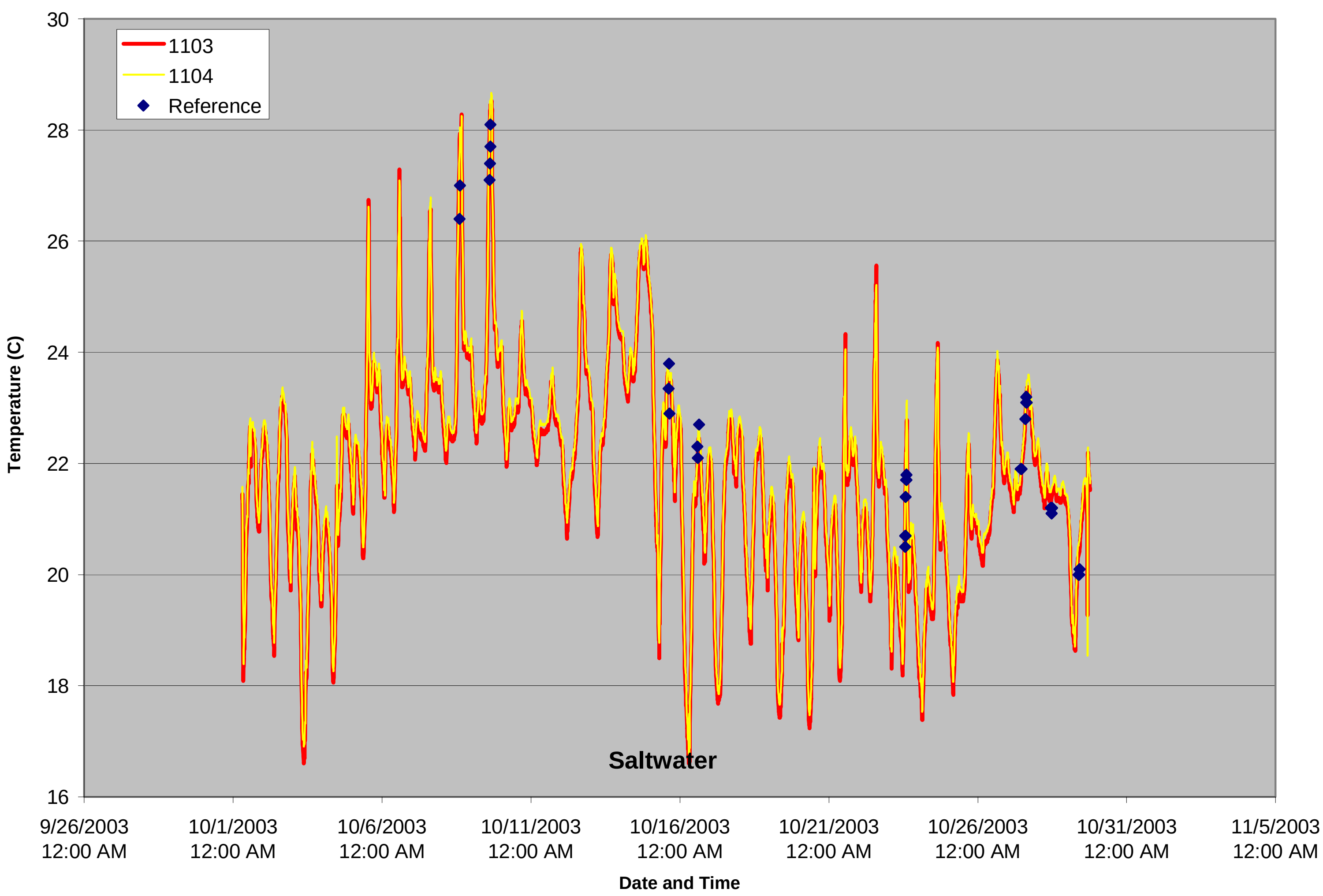


Figure 6-8a. Inter-Unit Reproducibility Data for Temperature During Saltwater Tests

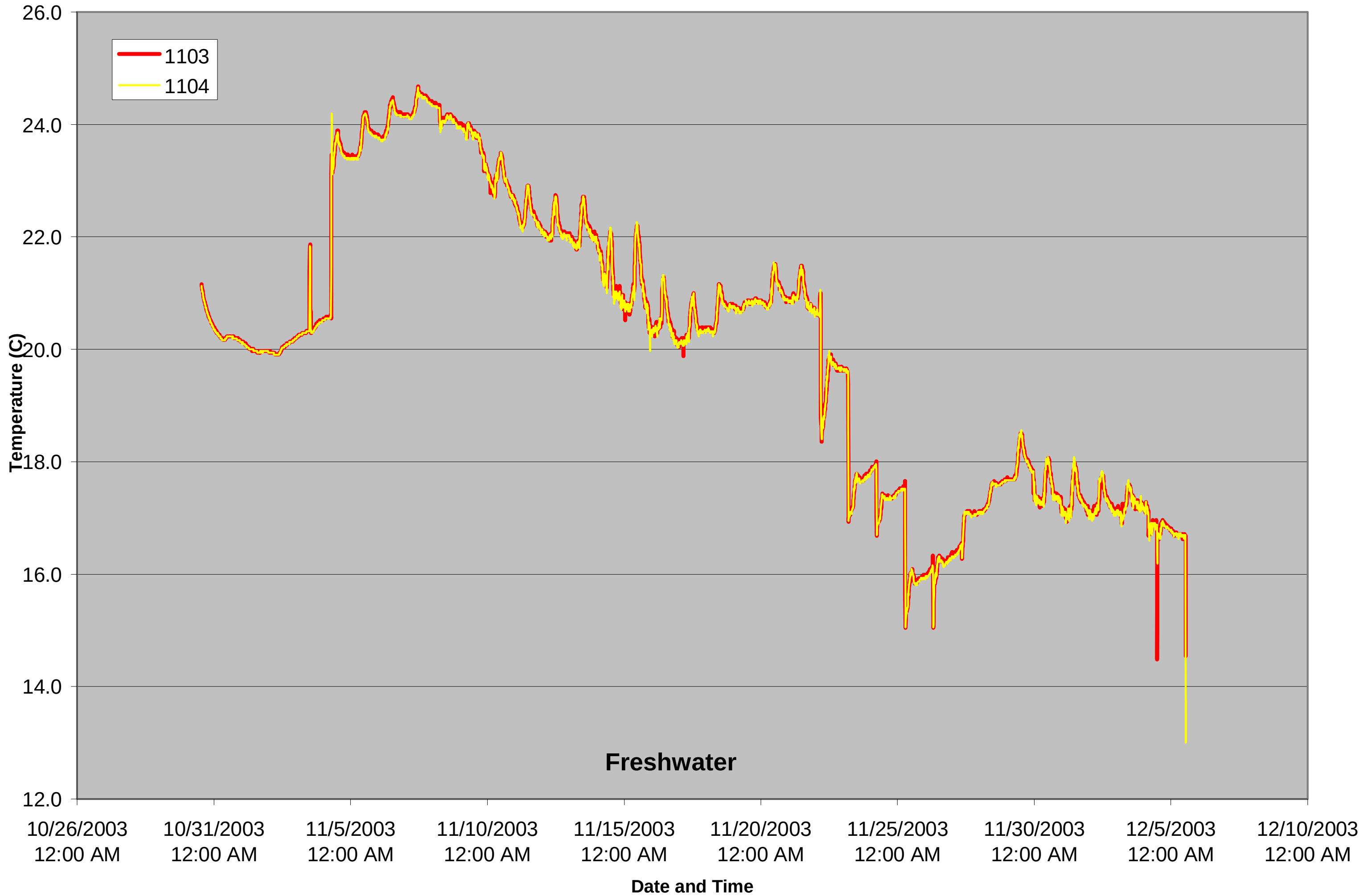


Figure 6-8b. Inter-Unit Reproducibility Data for Temperature During Freshwater Tests

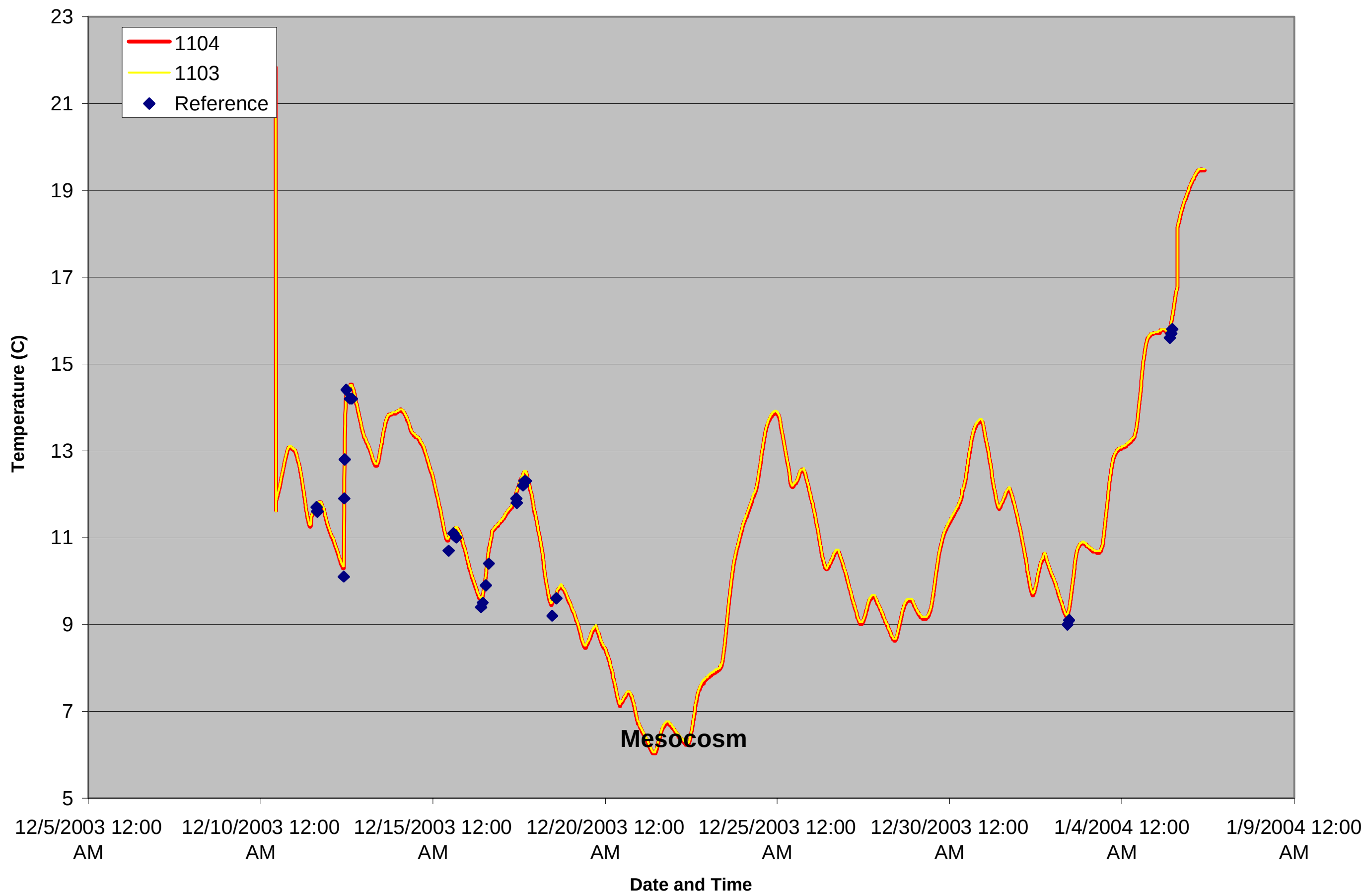


Figure 6-8c. Inter-Unit Reproducibility Data for Temperature During Mesocosm Tests

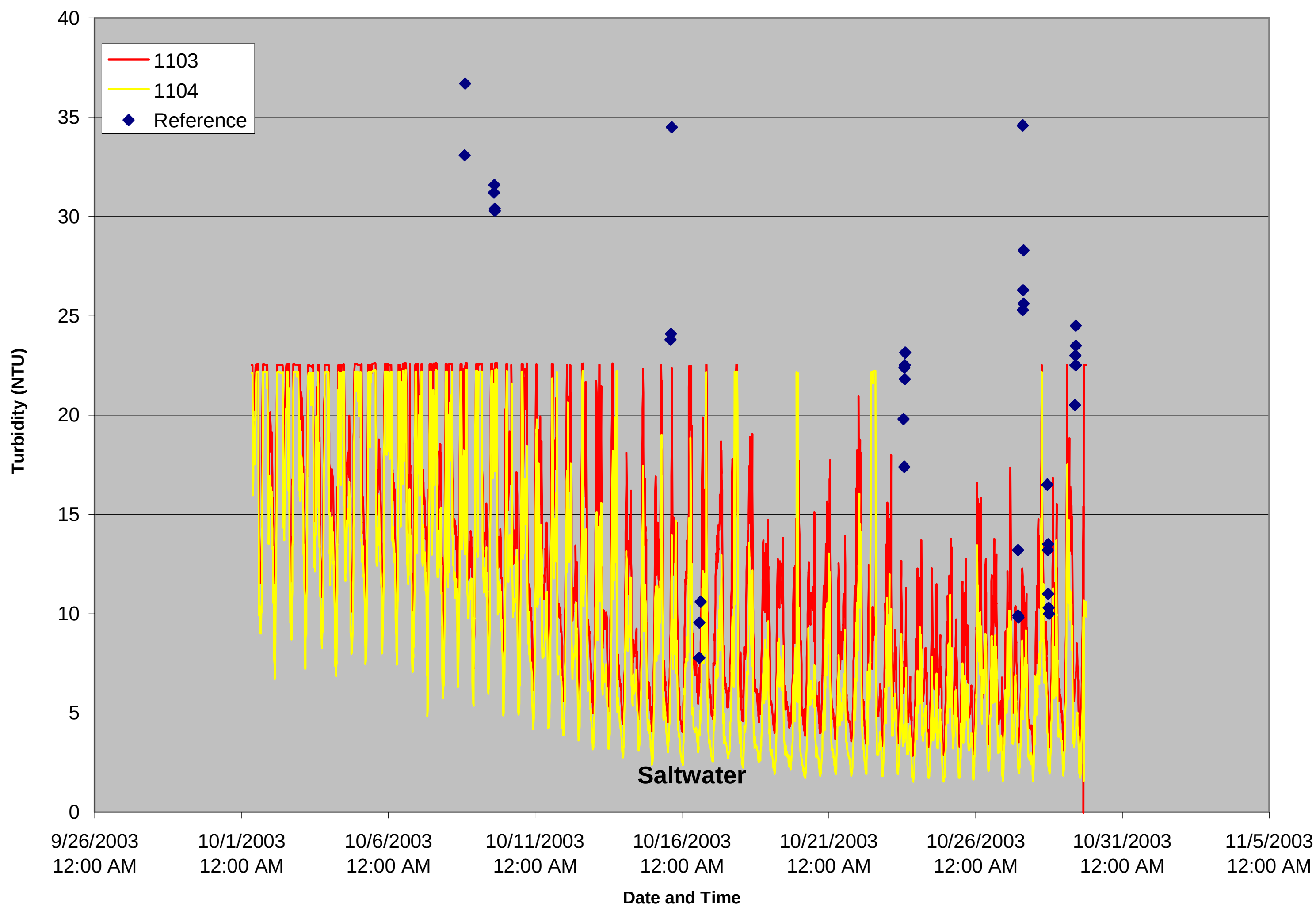


Figure 6-9a. Inter-Unit Reproducibility Data for Turbidity During Saltwater Tests

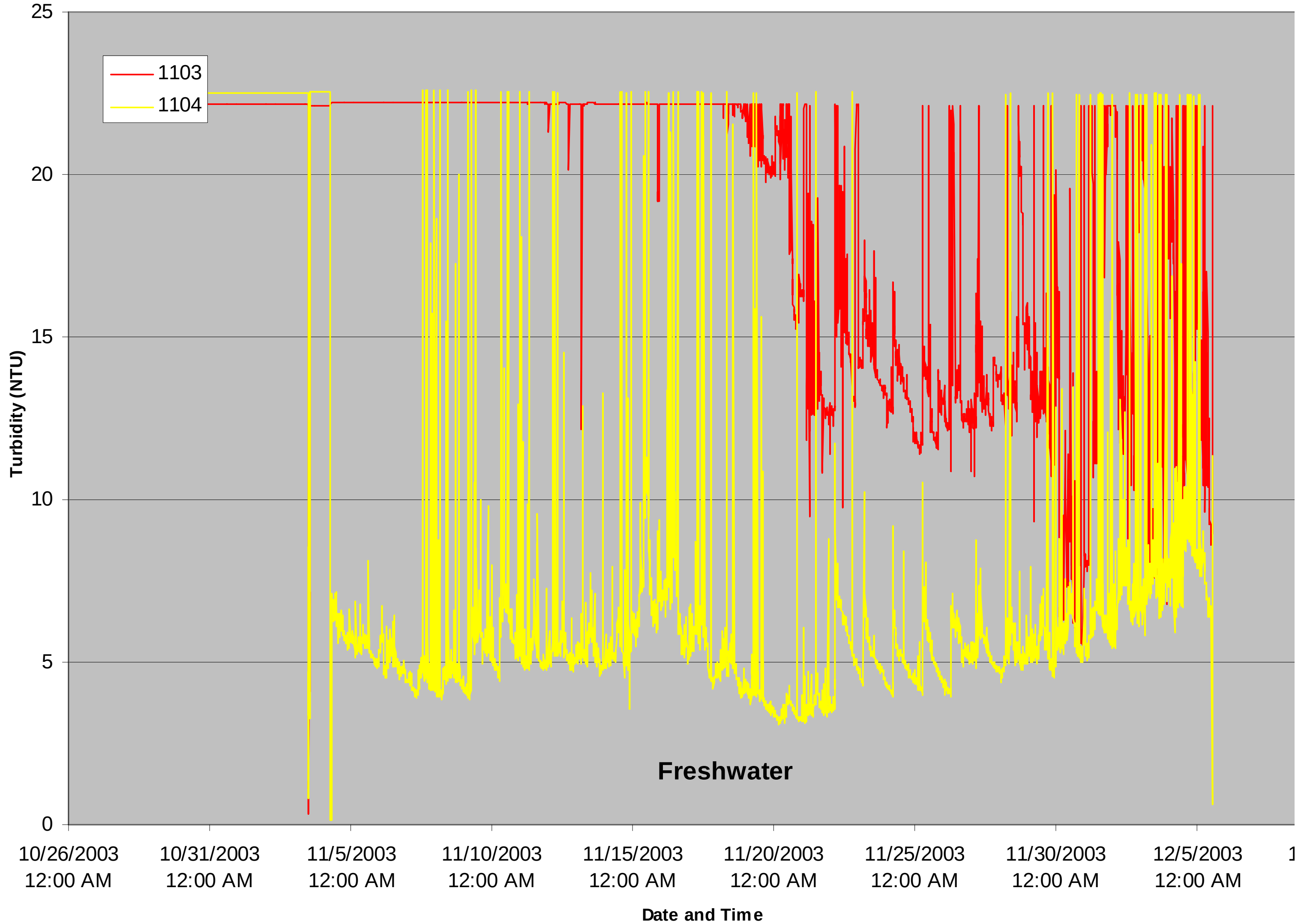


Figure 6-9b. Inter-Unit Reproducibility Data for Turbidity During Freshwater Tests

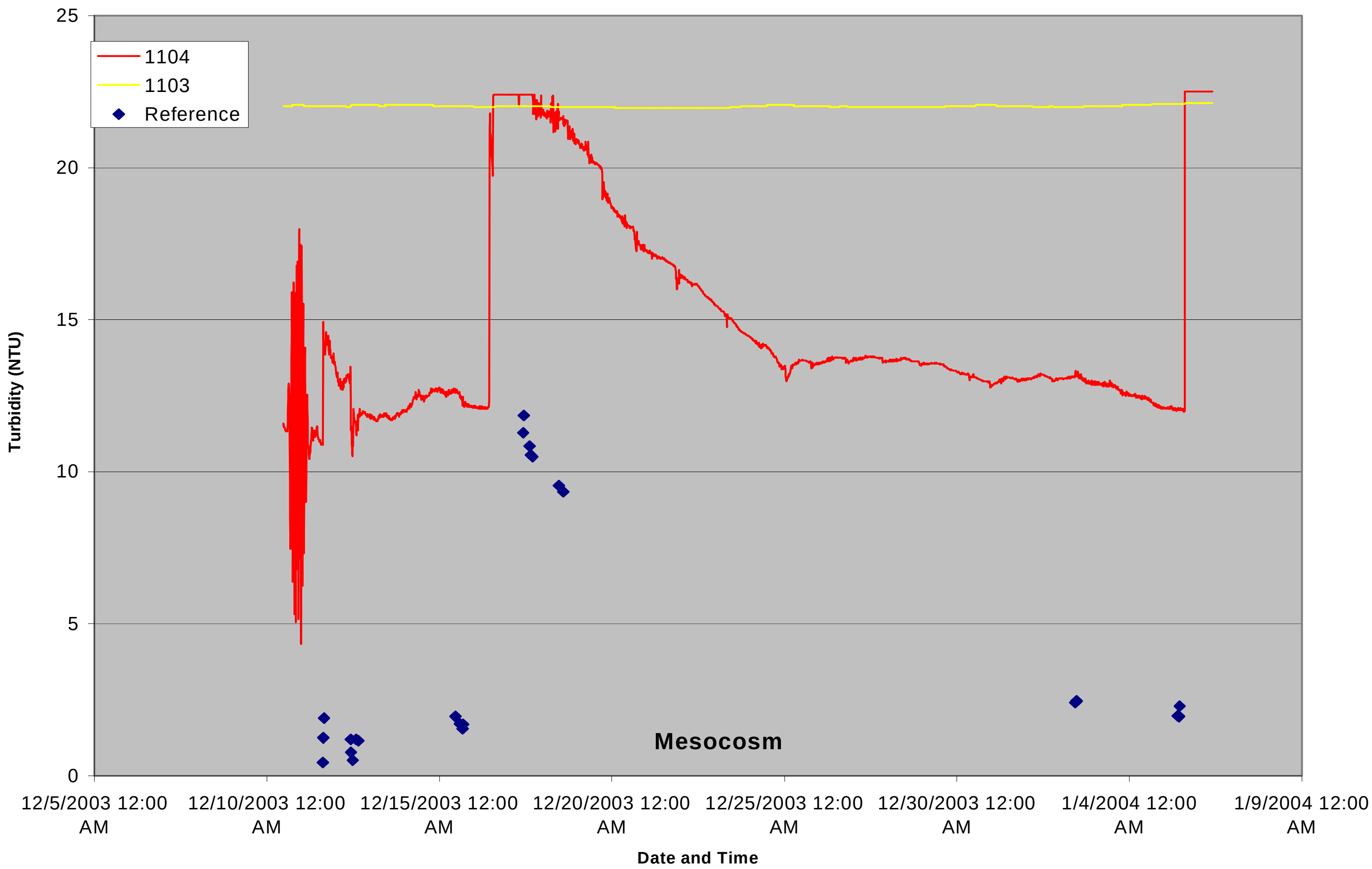


Figure 6-9c. Inter-Unit Reproducibility Data for Turbidity During Mesocosm Tests

6.6 Other Factors

6.6.1 Ease of Use

The Mk II with Optode 3830 was installed and deployed by CCHEBR staff with the oversight of AANDERAA during installation and Battelle during deployment. Once the Mk II with Optode 3830s were deployed, the vendor adopted a "hands off" approach for the remainder of the test. No maintenance was required. Data were collected to a personal computer by removing the data storage unit (DSU) from the Mk II with Optode 3830 and plugging it into a serial cable supplied by the vendor. AANDERAA-supplied software (Data Reading Program 5059, Version 1.00 build 84) was used to communicate with the DSU, which performed without a problem. The software allowed the data to be converted to ASCII format for inclusion in external data processing software. A sample printout from the software is shown in Appendix A. The Mk II with Optode 3830 required minimal interaction by operators during the test. Those interactions that did occur are described in Table 6-5.

Table 6-5. Installation, Operation, and Maintenance Activities

Date	Service Time	Activity
10/1/2003	—	Vendor representatives arrived on site.
10/2/2003	—	Mk II with Optode 3830 deployed.
10/30/2003	—	Mk II with Optode 3830 collected.
10/31/2003	60 minutes	Data downloaded.
11/4/2003	—	Mk II with Optode 3830 deployed.
12/8/2003	—	Mk II with Optode 3830 collected.
12/8/2003	60 minutes	Data downloaded.
12/10/2003	—	Mk II with Optode 3830 deployed.
1/5/2004	—	Mk II with Optode 3830 collected.
1/5/2004	15 minutes	Data downloaded.
1/5/2004	—	End of test.
Total	135 minutes	

6.6.2 Data Completeness

All of the required data were recorded during this verification. The two Mk II with Optode 3830s submitted for this test collected data at 10-minute intervals from October 1, 2003, until January 5, 2004, without any interruption in data collection. One hundred percent of the required data was collected by the Mk II with Optode 3830.

Chapter 7
Performance Summary

Two Mk II with Optode 3830s were evaluated in saltwater, freshwater, and mesocosm environments between October 2, 2003, and January 5, 2004. These Mk II with Optode 3830s measured DO, temperature, and turbidity in water at 10-minute intervals throughout these deployments. Table 7-1 summarizes the performance of the Mk II with Optode 3830s.

Table 7-1. Summary of Performance

Statistical Measure	**Parameter**	**1103**			**1104**		
		Saltwater	**Freshwater**	**Mesocosm**	**Saltwater**	**Freshwater**	**Mesocosm**
Calibration check accuracy[a]	DO (%)	98.9	98.9	99.7	97.3	95.6	83.9
	Turbidity (%)	30	1,500	NA[b]	18	800	520
Average relative bias[c]	DO (%)	-19.7	–[d]	-6.79	-13.8	–[d]	6.61
	Temperature (%)	-0.99	–[d]	-1.76	-1.76	–[d]	-1.51
	Turbidity (%)	54.2	–[d]	-521	69.0	–[d]	-452
		1103			**1104**		
Average precision	DO (%RSD)	1.32			0.73		
	Temperature (%RSD)	2.20			2.80		
	Turbidity (%RSD)	26.8			24.4		
Linearity		Best agreement between readings and reference values was for temperature. During the saltwater deployment, the DO measurements resulted in slopes between 0.70 and 0.74 and regression coefficients between 0.76 and 0.79 over a range of 3 to 6 mg/L. During the mesocosm deployment, slopes and regression coefficients both decreased. Finally, when the Mk II was within its range, the turbidity measurements resulted in a slope of 0.99 and a regression coefficient of 0.93 over a range of 0.4 to 15 NTU.					
		Average Difference Between 1103 and 1104 Readings					
		Saltwater		**Freshwater**		**Mesocosm**	
Inter-unit reproducibility	DO (mg/L)	1.02		1.42		1.78	
	Temperature (°C)	0.16		0.04		0.03	
	Turbidity (NTU)	3.12		10.9		7.26	

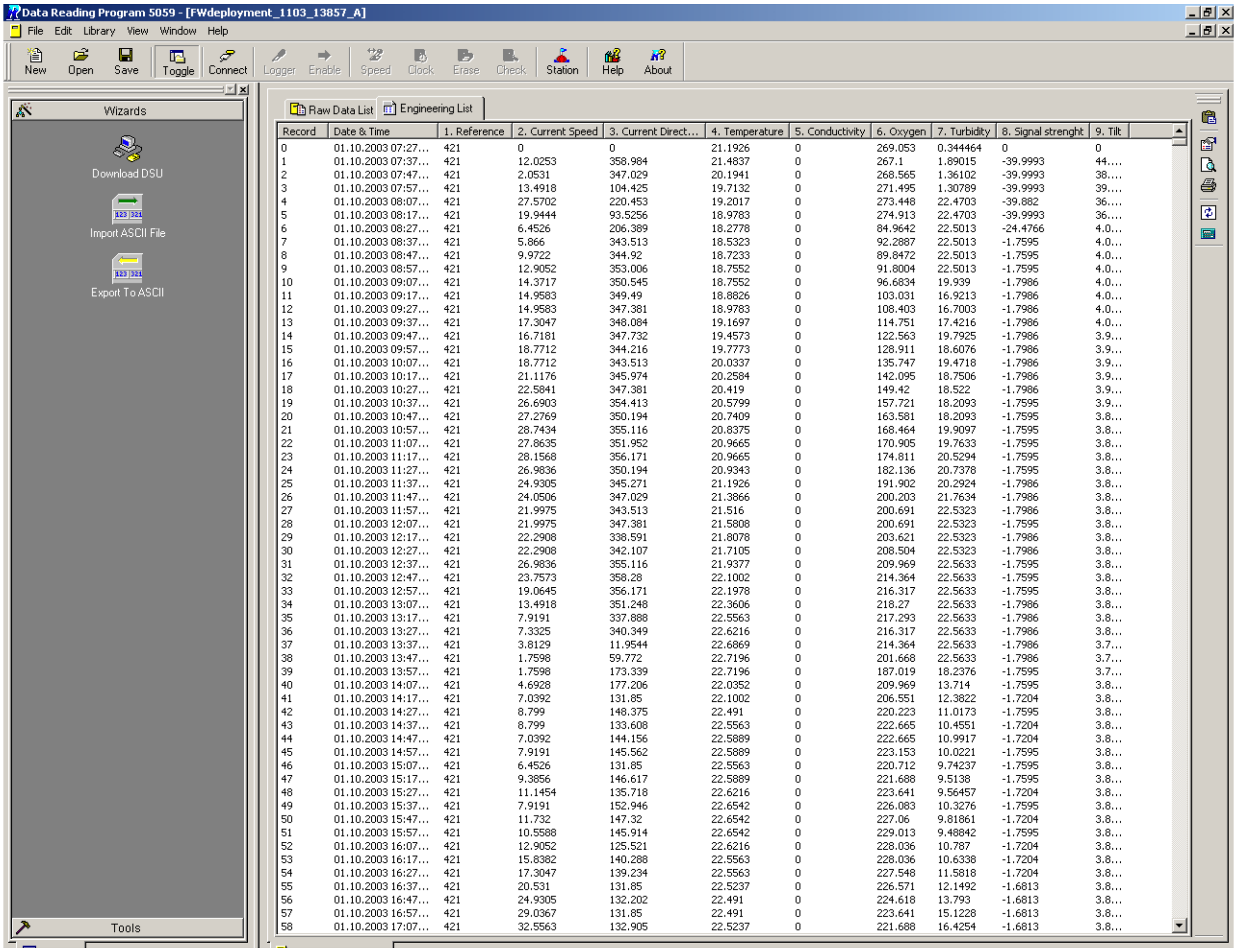
(a) The closer the percentage is to 100, the better.
(b) Saturated; no data reported.
(c) The closer the percentage is to zero, the better
(d) Stratification; no data reported.

Chapter 8
References

1. *Test/QA Plan for Long-Term Deployment of Multi-Parameter Water Quality Probes/Sondes,* Battelle, Columbus, Ohio, Version 1.0, May 2002.

2. *Quality Management Plan (QMP) for the ETV Advanced Monitoring Systems Center*, Version 4.0, U.S. EPA Environmental Technology Verification Program, Battelle, Columbus, Ohio, December 2002.

Appendix A
Sample Printout
Data Reading Program 5059



Record	Date & Time	1. Reference	2. Current Speed	3. Current Direct...	4. Temperature	5. Conductivity	6. Oxygen	7. Turbidity	8. Signal strenght	9. Tilt
0	01.10.2003 07:27...	421	0	0	21.1926	0	269.053	0.344464	0	0
1	01.10.2003 07:37...	421	12.0253	358.984	21.4837	0	267.1	1.89015	-39.9993	44....
2	01.10.2003 07:47...	421	2.0531	347.029	20.1941	0	268.565	1.36102	-39.9993	38....
3	01.10.2003 07:57...	421	13.4918	104.425	19.7132	0	271.495	1.30789	-39.9993	39....
4	01.10.2003 08:07...	421	27.5702	220.453	19.2017	0	273.448	22.4703	-39.882	36....
5	01.10.2003 08:17...	421	19.9444	93.5256	18.9783	0	274.913	22.4703	-39.9993	36....
6	01.10.2003 08:27...	421	6.4526	206.389	18.2778	0	84.9642	22.5013	-24.4766	4.0...
7	01.10.2003 08:37...	421	5.866	343.513	18.5323	0	92.2887	22.5013	-1.7595	4.0...
8	01.10.2003 08:47...	421	9.9722	344.92	18.7233	0	89.8472	22.5013	-1.7595	4.0...
9	01.10.2003 08:57...	421	12.9052	353.006	18.7552	0	91.8004	22.5013	-1.7595	4.0...
10	01.10.2003 09:07...	421	14.3717	350.545	18.7552	0	96.6834	19.939	-1.7986	4.0...
11	01.10.2003 09:17...	421	14.9583	349.49	18.8826	0	103.031	16.9213	-1.7986	4.0...
12	01.10.2003 09:27...	421	14.9583	347.381	18.9783	0	108.403	16.7003	-1.7986	4.0...
13	01.10.2003 09:37...	421	17.3047	348.084	19.1697	0	114.751	17.4216	-1.7986	4.0...
14	01.10.2003 09:47...	421	16.7181	347.732	19.4573	0	122.563	19.7925	-1.7986	3.9...
15	01.10.2003 09:57...	421	18.7712	344.216	19.7773	0	128.911	18.6076	-1.7986	3.9...
16	01.10.2003 10:07...	421	18.7712	343.513	20.0337	0	135.747	19.4718	-1.7986	3.9...
17	01.10.2003 10:17...	421	21.1176	345.974	20.2584	0	142.095	18.7506	-1.7986	3.9...
18	01.10.2003 10:27...	421	22.5841	347.381	20.419	0	149.42	18.522	-1.7986	3.9...
19	01.10.2003 10:37...	421	26.6903	354.413	20.5799	0	157.721	18.2093	-1.7595	3.9...
20	01.10.2003 10:47...	421	27.2769	350.194	20.7409	0	163.581	18.2093	-1.7595	3.8...
21	01.10.2003 10:57...	421	28.7434	355.116	20.8375	0	168.464	19.9097	-1.7595	3.8...
22	01.10.2003 11:07...	421	27.8635	351.952	20.9665	0	170.905	19.7633	-1.7595	3.8...
23	01.10.2003 11:17...	421	28.1568	356.171	20.9665	0	174.811	20.5294	-1.7595	3.8...
24	01.10.2003 11:27...	421	26.9836	350.194	20.9343	0	182.136	20.7378	-1.7595	3.8...
25	01.10.2003 11:37...	421	24.9305	345.271	21.1926	0	191.902	20.2924	-1.7986	3.8...
26	01.10.2003 11:47...	421	24.0506	347.029	21.3866	0	200.203	21.7634	-1.7986	3.8...
27	01.10.2003 11:57...	421	21.9975	343.513	21.516	0	200.691	22.5323	-1.7986	3.8...
28	01.10.2003 12:07...	421	21.9975	347.381	21.5808	0	200.691	22.5323	-1.7595	3.8...
29	01.10.2003 12:17...	421	22.2908	338.591	21.8078	0	203.621	22.5323	-1.7986	3.8...
30	01.10.2003 12:27...	421	22.2908	342.107	21.7105	0	208.504	22.5323	-1.7986	3.8...
31	01.10.2003 12:37...	421	26.9836	355.116	21.9377	0	209.969	22.5633	-1.7595	3.8...
32	01.10.2003 12:47...	421	23.7573	358.28	22.1002	0	214.364	22.5633	-1.7595	3.8...
33	01.10.2003 12:57...	421	19.0645	356.171	22.1978	0	216.317	22.5633	-1.7595	3.8...
34	01.10.2003 13:07...	421	13.4918	351.248	22.3606	0	218.27	22.5633	-1.7986	3.8...
35	01.10.2003 13:17...	421	7.9191	337.888	22.5563	0	217.293	22.5633	-1.7986	3.8...
36	01.10.2003 13:27...	421	7.3325	340.349	22.6216	0	216.317	22.5633	-1.7986	3.8...
37	01.10.2003 13:37...	421	3.8129	11.9544	22.6869	0	214.364	22.5633	-1.7986	3.7...
38	01.10.2003 13:47...	421	1.7598	59.772	22.7196	0	201.668	22.5633	-1.7986	3.7...
39	01.10.2003 13:57...	421	1.7598	173.339	22.7196	0	187.019	18.2376	-1.7595	3.7...
40	01.10.2003 14:07...	421	4.6928	177.206	22.0352	0	209.969	13.714	-1.7595	3.8...
41	01.10.2003 14:17...	421	7.0392	131.85	22.1002	0	206.551	12.3822	-1.7204	3.8...
42	01.10.2003 14:27...	421	8.799	148.375	22.491	0	220.223	11.0173	-1.7595	3.8...
43	01.10.2003 14:37...	421	8.799	133.608	22.5563	0	222.665	10.4551	-1.7204	3.8...
44	01.10.2003 14:47...	421	7.0392	144.156	22.5889	0	222.665	10.9917	-1.7204	3.8...
45	01.10.2003 14:57...	421	7.9191	145.562	22.5889	0	223.153	10.0221	-1.7595	3.8...
46	01.10.2003 15:07...	421	6.4526	131.85	22.5563	0	220.712	9.74237	-1.7595	3.8...
47	01.10.2003 15:17...	421	9.3856	146.617	22.5889	0	221.688	9.5138	-1.7595	3.8...
48	01.10.2003 15:27...	421	11.1454	135.718	22.6216	0	223.641	9.56457	-1.7204	3.8...
49	01.10.2003 15:37...	421	7.9191	152.946	22.6542	0	226.083	10.3276	-1.7595	3.8...
50	01.10.2003 15:47...	421	11.732	147.32	22.6542	0	227.06	9.81861	-1.7204	3.8...
51	01.10.2003 15:57...	421	10.5588	145.914	22.6542	0	229.013	9.48842	-1.7595	3.8...
52	01.10.2003 16:07...	421	12.9052	125.521	22.6216	0	228.036	10.787	-1.7204	3.8...
53	01.10.2003 16:17...	421	15.8382	140.288	22.5563	0	228.036	10.6338	-1.7204	3.8...
54	01.10.2003 16:27...	421	17.3047	139.234	22.5563	0	227.548	11.5818	-1.7204	3.8...
55	01.10.2003 16:37...	421	20.531	131.85	22.5237	0	226.571	12.1492	-1.6813	3.8...
56	01.10.2003 16:47...	421	24.9305	132.202	22.491	0	224.618	13.793	-1.6813	3.8...
57	01.10.2003 16:57...	421	29.0367	131.85	22.491	0	223.641	15.1228	-1.6813	3.8...
58	01.10.2003 17:07...	421	32.5563	132.905	22.5237	0	221.688	16.4254	-1.6813	3.8...